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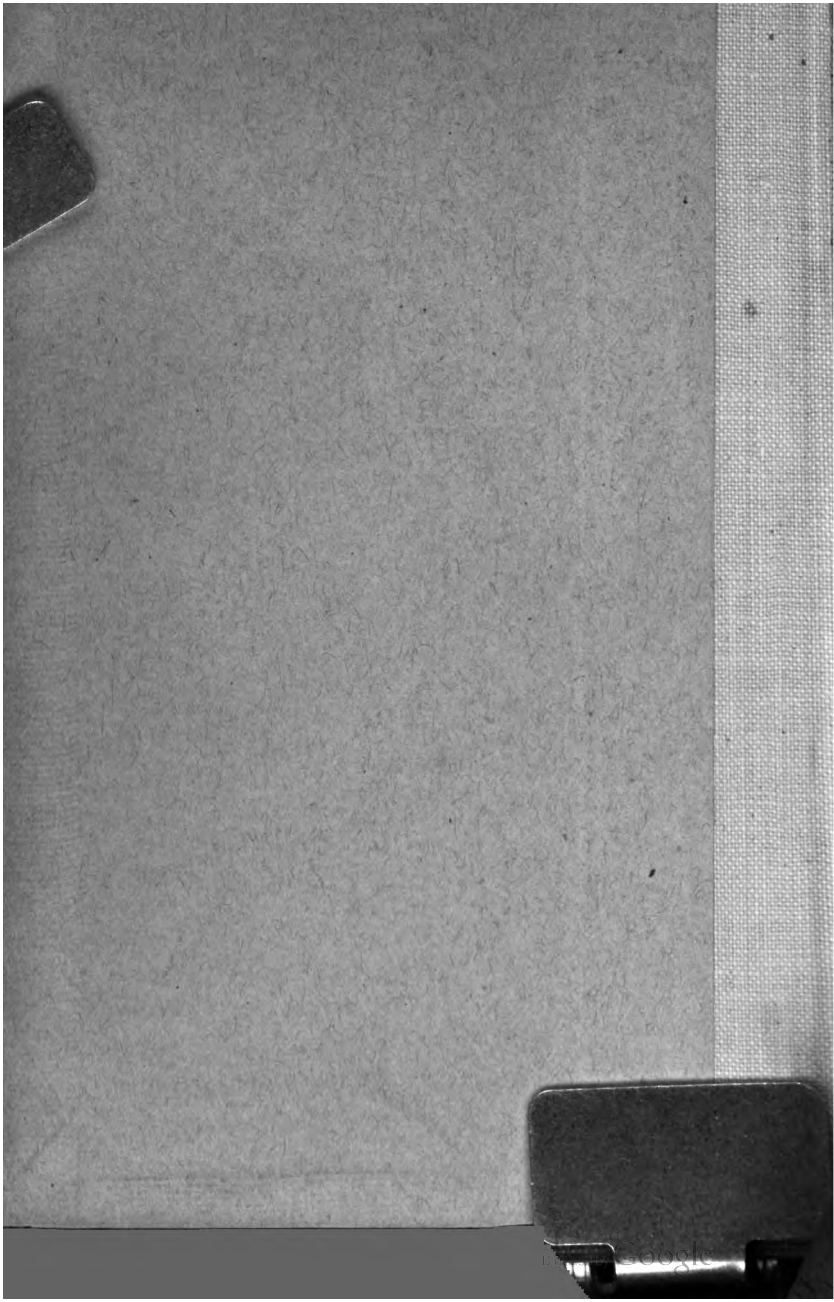
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Practical physical chemistry

James Brierley
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**PRACTICAL
PHYSICAL CHEMISTRY**

PRACTICAL PHYSICAL CHEMISTRY

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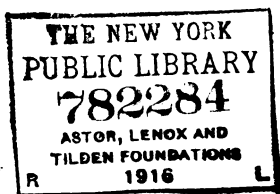
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PREFACE

DURING recent years it has come to be more widely recognized in the various schools of chemistry that a study of physical chemistry is necessary for all those who wish to study chemistry with any degree of thoroughness.

The theoretical significance of physico-chemical constants, and the fact that they find their application in almost every branch of chemistry, renders it essential for all students of the science to become familiar—to some extent, at any rate—with physico-chemical methods.

It is not possible within the limits of a small volume such as this to deal with every phase of the subject. I have, therefore, chosen such experiments as will demonstrate the fundamentals of the subject, in order that, in the first place, the student may familiarize himself with physico-chemical measurements, and secondly, that he may fix more firmly in his memory the knowledge that he has already gained in the lecture theatre. If a science is to really live, it is essential that theory and practice should go hand in hand. One principle demonstrated by the student himself is of far more value to the student than pages of lecture notes.

The importance of spectrum analysis seems to have been overlooked in the past, but it is the opinion of the author that the student should at least be familiar with the principal features of the subject, such as “mapping of spectra” and “determination of wave-lengths,” etc.; therefore a short chapter on this subject finds a place in the present volume.

Short chapters of Electrochemical Analysis, Electrolytic Preparations, have also been included, because, besides their purely academic value, they have their industrial applications.

I have thought it necessary, in certain sections at any rate, to introduce just sufficient theory to enable the student to understand the principles of his experiment, because, owing to the fact that many experiments require special apparatus, it is not possible for all the students to do the same experiment at the same time, and it frequently happens that a student's practical work is in advance of his theory. Hence the introduction of a little theory prevents the experiment becoming mechanical.

It will not be usually possible for students to perform experiments in all the sections, nor is it possible to say what sections should be omitted where the time is limited, because so much will depend upon the particular requirements of the student. For example, it may seem advisable for a student who intends to pursue certain industrial work to study thoroughly electro-analysis, electrolytic preparations, etc., at the expense of some of the more academic sections. Therefore, the actual experiments selected must be left to the discretion of the demonstrator.

In every case the student should read up the corresponding section in some theoretical textbook as soon as possible. Senter's "Outlines of Physical Chemistry" admirably meets the requirements of most students.

A slight knowledge of advanced mathematics (elements of calculus, etc.) has been assumed.

It is not possible to acknowledge all the textbooks which have assisted in compiling the present volume, but, in conclusion, I should like to acknowledge my indebtedness to Ostwald-Luther's "Physical Chemistry Measurements," Traube's "Physicochemical Methods," Elbs' "Electrolytic Preparations," Watts' "Spectroscopy."

J. B. F.

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NEWCASTLE-ON-TYNE
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INTRODUCTION

The Balance : Rules for Weighing—The balance should be placed so that it is protected from direct rays of the sun or other sources of heat, which would produce inequality of temperature in the different parts. It should rest on a firm bench, which is free from vibration.

The balance must be kept horizontal by means of the foot screws. This position is indicated by a spirit-level or plumb-line.

The interior of the balance case should be kept dry by means of calcium chloride, etc.

The weights should be placed on the pan only *after the arrestment of the beam*, picking up the weights in all cases by means of forceps. Rapid swinging of the beam is not conducive to accurate weighing, and the final weighings should be made with the case closed.

Adjustment of the Balance—The sensibility, and hence the period of vibration, are regulated by means of a gravity bob, situated near the middle of the pointer. The adjustment is so made that the period of vibration for a short-armed balance is from six to ten seconds, and from ten to fifteen seconds for a long-armed balance.

The adjustment, so that the pointer swings equally on both sides of the middle division of the scale, is made by movable weights attached to the end of the beam; when these fail, the unsymmetrical weight in the middle of the beam is given such a position that the adjustment can be made.

Determination of the Zero-Point—It is not necessary nor desirable in weighing that the weights be so adjusted, so that the pointer will swing equal on both sides of the middle

division of the scale. The actual resting-point is determined from the several turning-points of the pointer.

The zero is determined by releasing the beam and allowing it to swing freely (free from any load). Then, neglecting the first swing, observe the extreme points on the scale, taking two readings on one side, and one on the other. Suppose the readings on the right are called positive, and those on the left negative, and the readings on the right were $+6.5$ and $+5.6$, and the reading on the left -5.8 , then the mean reading on the right was $+6.01$, and the zero will be halfway between $+6.01$ and -5.8 —i.e., $+0.10$, that is, 0.1 of a division to the right. It frequently happens that this zero changes after the weighing of heavy loads, therefore it must be frequently redetermined.

As before mentioned, it is not desirable to have to adjust the weights so that the pointer moves "symmetrically" about this zero; such a process would be tedious, and is absolutely unnecessary. To avoid this the *sensibility* of the balance is determined. By the *sensibility* of a balance is meant the *change of position* of the zero, for an increase of 1 mgm. on one side of the balance.

The weighing on the pan is only made to within 1 cgm., the milligrams being determined by means of a rider working on a graduated beam. Suppose, when the weight has been practically determined, the resting-point calculated from the swings is 2.40 . Now move the rider so as to increase the weights by, say, 2 mgms., and the resting-point now be -1.8 . The resting-point has moved through 4.2 divisions for a change of 2 mgms.—i.e., 2.1 divisions for 1 mgm. This is the *sensibility* of the balance for the load used. The *sensibility* changes, however, with the load, and it is therefore necessary to determine the *sensibility* for different loads, say for every 10 grams. Then plot a curve so that the *sensibility* can be determined for any load; plot the loads as abscissæ and the corresponding *sensibilities* as ordinates.

Knowing the sensibility of the balance, it is possible to weigh to the fourth decimal place. Suppose the zero of a balance is found to be $+1$, and that in a certain weighing the resting-point is found to be $+1.5$, also let the sensibility for this particular load be 3.5 . In the weighing we have a change of resting-point of $+0.5$. Now, we know from the sensibility that 1 mgm. produces a change of 3.5 , hence a change of 0.5 is produced by $\frac{0.5}{3.5} = 0.14$ mgms. Thus, if the weights plus rider on the balance read 21.693 grams, the true weight is 21.69314 grams. It is usual to take the nearest fourth decimal place, as without additional precautions the fifth place is of no value.

Calibration of a Set of Weights—Let the larger set of weights be designated $50'$, $20'$, $10'$, $10''$, $5'$, $2'$, $1'$, $1''$, $1'''$.

Place the 50 -gram weight on the left-hand pan and exactly balance it by the others, the final adjustment being done by the method of oscillation. Then place the 50 -gram weight on the right-hand pan, and repeat the weighing. Suppose we have—

	Left.	Right.	
(1)	$50'$	$20' + 10' + 10'' + \dots + a$	$mg.$
(2)	$20' + 10' + 10'' + \dots + b$	$50'$	$mg.$

then $50' = 20' + 10' + 10'' + \dots + \frac{1}{2}(a + b)mg.$

Similarly we obtain—

$$20' = 10' + 10'' + \frac{1}{2}(c + d)mg.$$

$$10'' = 10' + \frac{1}{2}(e + f)mg.,$$

and so on.

Putting $\alpha, \beta, \gamma, \dots$ for $\frac{1}{2}(a + b), \frac{1}{2}(c + d), \frac{1}{2}(e + f)$ respectively, we get—

$$\begin{array}{rcl}
 50' & = & 20' + 10' + 10'' + \dots + \alpha \\
 20' & = & 10' + 10'' + \beta \\
 10'' & = & 10' + \gamma \\
 5' + 2' + 1' + 1'' + 1''' & = & 10' + \delta
 \end{array}$$

in which $\alpha, \beta, \gamma, \delta$, can be either positive or negative.

Then, comparing *all* weights against the 10'-gram weight, we have—

$$50' = 5 \times 10' + \alpha + \beta + 2\gamma + \delta$$

$$20' = 2 \times 10' + \beta + \gamma$$

$$10'' = 1 \times 10' + \gamma$$

$$10' = 10'$$

$$5' + 2' + 1' + 1'' \times 1''' = 1 \times 10' + \delta$$

$$S = 50' + 20' + 10' + 10'' + 5' + 2' + 1' + 1'' + 1''' = 10 \times 10' + \alpha + 2\beta + 4\gamma + 2\delta$$

$$\therefore S = 100 \text{ grams} = 10 \times 10' + (\alpha + 2\beta + 4\gamma + 2\delta)$$

$$\text{Let } \frac{1}{10} (\alpha + 2\beta + 4\gamma + 2\delta) = \sigma, \text{ then}$$

$$10' = 10 \text{ grams} - \sigma$$

$$10'' = 10 \text{ grams} = \sigma + \gamma$$

$$5' + 2' + 1' + 1'' + 1''' = 10 \text{ grams} - \sigma + \delta$$

$$20' = 20 \text{ grams} - 2\sigma + \beta + \gamma$$

$$50' = 50 \text{ grams} - 5\sigma + \alpha + \beta + 2\gamma + \delta.$$

The actual values of α , β , γ , etc., have been determined during the weighing, and can here be substituted in the above.

In a similar manner the 5', 2', 1', 1'', 1''' are compared with each other, and also the fractional weights. From the values thus obtained a table showing the exact value of each weight should be made.

PRACTICAL PHYSICAL CHEMISTRY

CHAPTER I THERMOSTATS

IN order to perform many of the experiments described in the present volume, it is necessary that the whole of the materials used should remain at a constant and definite temperature throughout the duration of the experiment. This is usually accomplished by immersing the apparatus and its contents, or such portions as may be necessary, in a bath usually of water, the heating (or cooling) of which can be so automatically controlled so that the temperature remains constant within certain narrow limits for an indefinite period, or at any rate for the duration of any experiment. A bath which is so regulated is known as a *thermostat*.

The nature of the bath may vary according to the requirements of the experiment. In some cases a large-sized beaker will suffice, but usually a sheet copper (or galvanized iron) tank, about 60 cms. $\times$ 60 cms. $\times$ 60 cms., is used. Very often a cylindrical bath of similar dimensions is used instead of a cubical bath. In cases where it is necessary to observe the apparatus during an experiment, a thermostat in which a sheet of glass has been let in on opposite sides is used. But very often for such experiments a large beaker or an inverted bell jar may be conveniently substituted. The copper or iron bath should be covered on the outside with a layer of felt.

Thermo-Regulators—The heating of the bath is usually effected by means of a gas flame. But it is obvious that once the bath has attained the required temperature, the function of the flame is to counterbalance all loss of heat from such causes as radiation, evaporation, etc., which is by no means a constant factor. Hence it is necessary to automatically

control the flame ; this is done by means of a *thermo-regulator*. Two useful types are shown in Fig. 1. The bulb portion *A* is filled with some liquid which has a high coefficient of expansion, and at the same time a fairly high boiling-point. Toluene is very suitable for the purpose. The rest of the apparatus is filled with mercury up to tube *B*, which is of small bore, in order to increase the sensitiveness of the regulator. The gas passes in through tube *C*, which is fixed to

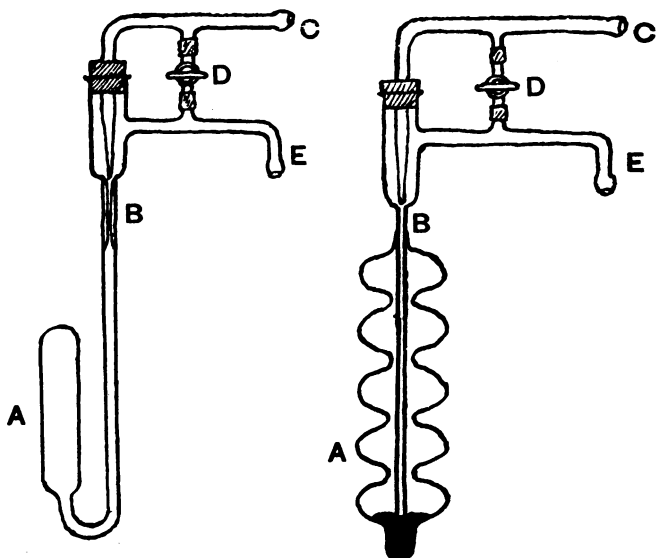


FIG. 1

the top of the regulator tube by a cork, and thence through *E* to the burner. If the temperature of the bath gets too high, the toluene expands, drives the mercury up the tube *B*, and closes the inlet tube *C*, thus cutting off the gas-supply. To prevent the flame being extinguished, a certain amount of gas passes to the burner by means of the by-pass *D*, the actual amount of gas passing being controlled by a stop-cock or clip, and it is arranged that the desired temperature is almost maintained when *C* is closed.

To fill and adjust the Regulator—Remove tube *C* and fit a glass tube *H*; connect this by means of rubber tubing (pressure tubing), provided with a pinch-cock, *F*, to a pump. Connect a short length of glass tubing to *E*, provided also with a pinch-cock. The glass tube dips into a beaker of toluene (see Fig. 2). Now close the pinch-cock at *G* and exhaust the apparatus by means of the pump; then close the pinch-cock *F* and open the pinch-cock on *G*, when toluene will

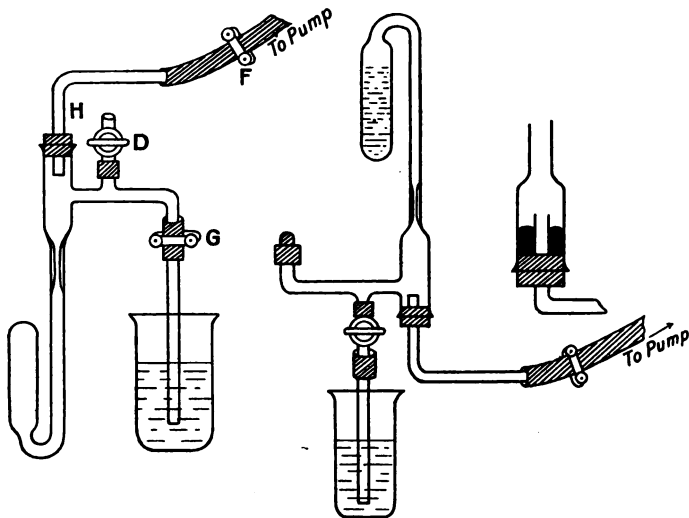


FIG. 2

be drawn into the apparatus. Now invert the regulator and again exhaust, and again admit toluene until only a small amount of air remains. Again exhaust and pour over the bulb of the regulator a stream of hot water, causing the toluene to vaporize, thus driving out most of the air; shut off the pump, and again admit toluene whilst cooling. There should still be left a small air space. Now remove the tube at *H* and introduce a quantity of mercury. Again invert the regulator so that the mercury resides round the tube *H* (see Fig. 2). Now exhaust while heating the bulb with hot water until all the air has been driven out. Now invert the regu-

lator, and on cooling the mercury will be drawn into the stem of the regulator. If a small bubble of air still persists, it can frequently be got rid of by slight shaking, and then allowing to stand, since toluene dissolves air to some extent. The excess of toluene which appears on the top of the mercury may be removed by a small roll of filter-paper. To adjust the quantity of mercury, place the regulator in a bath at the desired temperature. Then remove the mercury by means of a pipette (see Fig. 3) until the meniscus is just above the top of the capillary. If insufficient mercury has been added, heat

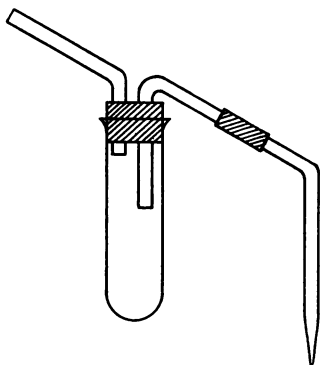


FIG. 3

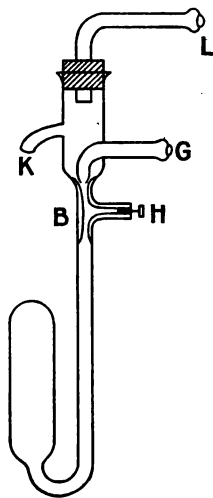


FIG. 4

up the bath until the mercury appears above the capillary, then add a little more, setting the regulator as before. The tube *C* is then put in position, so that at the temperature required it is just closed by the mercury. This position has usually to be found by trial. This regulator, when working properly, should be given a constant temperature with $\pm 0.1^\circ$.

For temperatures below that of the surroundings, a regulator as shown in Fig. 4 is used. It is filled just as in the case of the gas regulator. The adjustment of the mercury meniscus is made in this case by means of screw *H*. A slow

stream of ice-cooled water is admitted at *L*, and when the bath is below the desired temperature, the mercury in *B* falls, thus allowing the ice-cooled water to escape through *G* to waste. As the temperature rises the tube *G* is closed by the mercury, thus causing the iced water to escape through *K*, which runs into the bath. The rate at which the water enters through *L* must be so regulated that it can easily be carried away by tube *G* without any fear of it rising to the level of *K*. Owing to the gradual increase in the amount of water in the thermostat, the bath in this case must be provided with an overflow tube, which is connected with the sink.

In order to maintain a uniform temperature throughout the bath it is necessary to stir the water. This may be conveniently done by means of an air blast where the temperature of the bath is not too high. A piece of soft metal composition tubing, closed at one end, is bent in the form of a ring, and pierced at intervals of about a decimetre with small pinholes; this is connected with an air blast such as is produced by a water-blower. As the air escapes it stirs up the water. Where this is not possible, an ordinary stirrer may be used, to which a pulley and bearing is fitted. A convenient stirrer may be made from a bicycle hub, by replacing the axle by a longer steel rod, on one end of which is attached a screw clip, and on the other a pulley. A suitable form of stirrer can be fastened on by the screw clip, and the stirrer rotated by means of a small motor or hot air engine.

The thermo-regulator, the stirrer, and also a Beckmann thermometer, are supported within the bath by means of retort clamps fastened to the side. The regulator is then connected up with the gas-supply and with a small burner underneath the bath. For temperatures below 50° F. a suitable burner is obtained by removing the tube from an ordinary bunsen burner. For higher temperatures a bunsen fitted with a rose or gauze top may be used. The bath should initially be filled with water which has been heated to approximately the temperature required. For temperatures above 50° F. the water may be covered with a layer of oil, to prevent undue loss by evaporation.

For very high or very low temperatures, where constancy is required, the boiling-point of certain liquids is used; or the melting of certain solids. For suitable substances see Appendix.

CHAPTER II

DENSITY OF GASES, LIQUIDS, AND VAPOURS

Density of Gases and Vapours—Strictly, the density of a gas is the mass of unit volume—i.e., of 1 c.c.; but as gases are greatly influenced by temperature and pressure, density is defined as the mass of unit volume at N.T.P. It is, however, more convenient to determine the density of the gas relative to some standard whose density is taken as unity when measured under the same temperature and pressure. Hydrogen is frequently taken as the standard, but of late years oxygen = 32 has been suggested, since in chemistry the densities of gases are usually determined with a view to ascertaining their molecular weight; and as oxygen is now the standard for atomic weights, it is advisable to determine densities by this standard also.

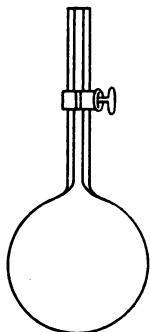


FIG. 5

To Determine the Absolute Density of Dry Oxygen—A clean dry bulb about 200 c.c. capacity, and fitted with a capillary tube and tap (see Fig. 5), is first calibrated by weighing it vacuous and then filled with water at a known temperature; then, by multiplying the weight of water by its density at that particular temperature, the volume of the bulb can be ascertained. (*Note*—in all weighing it is advisable to use a counterpoise of approximately the same weight and volume in order to eliminate errors due to the buoyancy of the air.) Having determined the volume of the bulb, it is now dried thoroughly and evacuated. Oxygen dried by passing through calcium chloride tubes is carefully admitted, the bulb being placed in a thermostat

during filling (Fig. 6), which should take at least five minutes, and the bulb again weighed.

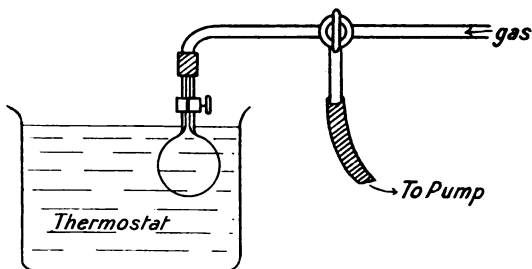


FIG. 6

If w is the weight of vacuous bulb and W the weight when full of oxygen, then $W - w = \text{weight of the oxygen}$.

If $V = \text{volume of the bulb}$, then—

$$V_o = \frac{V \times 273 \times p}{(273 + t) \times 760}$$

Hence the density of the gas will be—

$$= \frac{W - w}{V_o}$$

Since 1 gram molecule of a gas occupies 22400 c.c. at N.T.P., the molecular weight will be—

$$M = 22400 \times \frac{(W - w)}{V_o}$$

To Determine the Density of Carbon Dioxide Relative to Oxygen—Repeat the above experiment, weighing the bulb this time full of carbon dioxide. If the carbon dioxide is generated in a Kipp's apparatus, the bulb is filled under slight pressure; it is therefore necessary to open the tap for a second to allow the gas to come to atmospheric pressure.

In both the above experiments the bulb should be placed

in a thermostat during the filling, and should remain in at least five minutes before closing the tap.

Since the volume, temperature, and pressure, are the same for both gases, the relative density will be—

$$\frac{\Delta \text{ of CO}_2}{\Delta \text{ of O}_2} = \frac{\text{Weight of CO}_2}{\text{Weight of O}_2}.$$

Determination of Vapour Density (Victor Meyer's Method)—The commonest and most convenient method for the determination of the density of the vapour of a substance which is not a gas at ordinary temperatures is that due to Victor Meyer.

A definite quantity of substance is introduced into an air chamber, which is kept at a constant temperature (this temperature must be higher than the boiling-point of the substance to be tested). When the substance vaporizes it displaces its own volume of air, which is collected and measured at a known temperature and pressure (usually air temperature).

The apparatus (Fig. 7) consists of a cylindrical glass vessel, having near the top two side tubes, and closed with a rubber stopper lubricated with graphite. Through side tube *A* is fitted, by means of a rubber stopper, a short glass rod flattened at the end. Side tube *B*, through which the expelled air passes, leads into an inverted graduated glass cylinder over water (boiled). This glass vessel is surrounded by an outer jacket, in which some suitable liquid is boiled.

Details—Weigh out into a small stoppered tube or bulb a small quantity of the substance (*e.g.*, chloroform). Heat up the tube *C* with the vapour of some suitable liquid, until no more air is expelled from tube *B*. Then introduce the weighed substance through the top of the tube, so that it rests on the flattened part of the glass rod; see that all joints are tight; invert a graduated tube filled with water over the side tube, and then slightly twist the glass rod so that the tube falls to the bottom. (*Note*—the bottom should be protected with a wad of asbestos fibre.) Vaporization takes place, and equivalent volume of air is expelled. When no further air is expelled, the volume in the graduated tube is read off.

Calculation—Let V be the volume of air expelled,
 t the temperature of the air,
 p the barometric pressure,
 x the vapour pressure of water vapour at $t^{\circ}\text{C}$,
 w the weight of substance taken,
 h pressure due to column of water in graduated tube.

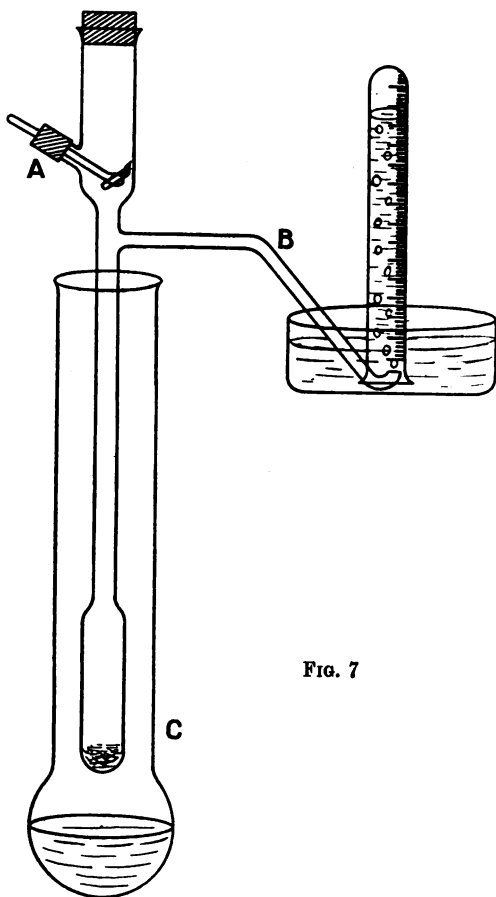


FIG. 7

The volume of air at N.T.P.—

$$V_o = \frac{V \times 273 \times (p - x - h)}{(t + 273) \times 760}.$$

Hence we get V_o , which is the volume which w grams of the substance would have if it were a vapour at N.T.P.

$$\therefore \text{Weight of 1 c.c. of vapour} = \frac{w}{V_o}.$$

$$\text{And the molecular weight} = 22400 \times \frac{w}{V_o}.$$

The density relative to some standard is found by dividing the weight of 1 c.c. of vapour by the weight of 1 c.c. of unit of gas (usually air or hydrogen).

Suitable heating substances are water, 100° ; aniline, 183° ; nitrobenzene, 211° ; diphenylamine, 300° ; paraffin bath, 350° ; sulphur, 448° C.

The heating liquid should have a boiling-point about 30° to 40° above the vaporizing-point of the substance.

Density of Liquids—The density of a liquid is the mass of unit volume. For liquids the mass of 1 c.c. of water at 4° C.

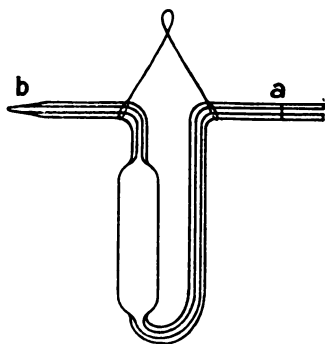


FIG. 8

is taken as the unit of mass. Hence the density of a liquid may be defined as the ratio of its mass to the mass of an equal volume of water at 4° C. The most convenient form of apparatus for determining the density of liquids is what is known as a "pycnometer" (Fig. 8). It consists essentially of a U tube; usually one limb is about 1.5 cms. diameter, and the other capillary 1 to 1.5 mm. bore. For accurate experiments the two ends of the tube are fitted with ground glass caps.

For ordinary purposes these may be omitted, except where very volatile liquids are used.

Prior to making a determination of the density of a liquid, the pycnometer should be thoroughly cleaned and dried. This may be conveniently done by washing successively with

distilled water, alcohol, and ether, and finally drawing a current of dry air through the tube. Heating the tube should be avoided, as it takes the tube some time to recover its normal volume after heating (from ten hours to several days).

The pyknometer is then weighed by suspending it from the beam of the balance with a double hook of platinum wire; then fill the pyknometer with cold, freshly distilled water. This is conveniently done by attaching a rubber tube to the capillary tube and placing the other end in the distilled water and sucking gently.

The pyknometer is then suspended in a thermostat, so that the two ends are just about 2 cms. above the level of the water in the thermostat.

When the water in the pyknometer has attained the temperature of the thermostat (about 20 mins.), the amount of water must be so adjusted that it fills the pyknometer to a definite mark on the capillary tube. If it is necessary to introduce a little water, this may be done by placing a tube carrying a drop of water against the end of the tube (*b*), when the water will be drawn in.

To remove any excess of water a small piece of filter-paper placed at *b* may be used. The successful adjustment of the meniscus to the mark *a* requires practice.

The pyknometer, which is now filled with a definite volume of distilled water at a definite temperature, is now removed from the thermostat, dried with a cloth, and carefully weighed. The pyknometer is then cleaned and dried as before, and filled with the liquid to be tested. The volume is adjusted in the thermostat exactly as before. The pyknometer is then dried with a cloth and weighed.

Calculation—The apparent weight of the liquid in air—

$$W_e = [(\text{pyknometer} + \text{liquid}) - (\text{pyknometer} + \text{air})].$$

The weight of an equal volume of water—

$$W_w = [\text{pyknometer} + \text{water}] - (\text{pyknometer} + \text{air}).$$

The approximate density is therefore—

$$\Delta_t^* = \frac{W_e}{W_w}.$$

This is usually all that is required.

The absolute density—i.e., at 4° C.—would be—

$$\Delta_{4^{\circ}}^r = \frac{W_e}{W_w} \times Q,$$

where Q is the density of water at t .

It is further necessary to correct for the buoyancy of the air; therefore for the final expression we get—

$$\begin{aligned} \Delta_{4^{\circ}}^r &= \frac{W_e}{W_w} \cdot Q - \frac{\lambda(W_e - W_w)}{W_w} \\ &= \frac{W_e}{W_w} (Q - \lambda) + \lambda, \end{aligned}$$

where λ is the average density of the air compared with water, and may be taken as 0.0012.

Experiment to Determine the Density of Ethyl Alcohol—Do this by the method described above.

Determination of the Specific Gravity at Higher Temperatures, and the Determination of the Molecular Volume of Liquids at Their Boiling-Points—The pycnometer used in this case is as indicated in Fig. 9. It consists of a thin Jena glass bulb about 3 c.c. capacity, united with a somewhat longer, narrow capillary tube with a turned-up end.

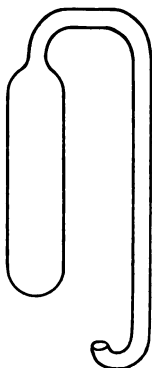


FIG. 9

The tube, cleaned and dried, is first weighed empty.

The pycnometer may be conveniently filled by alternately heating and cooling the bulb. Place the open capillary in a beaker of the liquid to be tested, and immerse the bulb in a hot bath; after a minute or so lift the bulb out of the bath, still keeping the capillary in the liquid. As the bulb cools, liquid will be drawn over. Repeat this several times, gradually raising the temperatures of the bath until only a very small bubble of air remains on cooling.

The almost filled pycnometer is suspended in a wide-mouthed boiling-flask by means of a platinum wire. The flask is also fitted with a reflux condenser and a thermometer.

The liquid in the flask is the same as in the pyknometer (see Fig. 10).

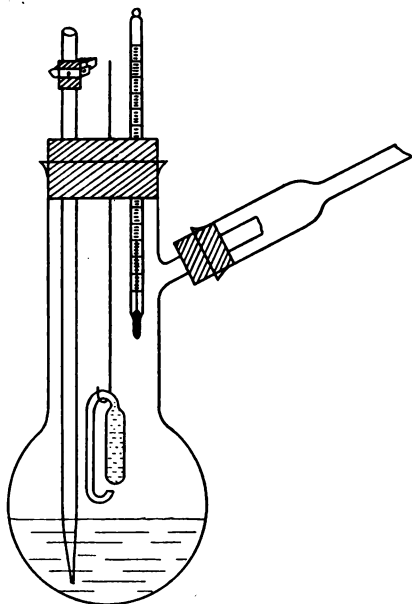


FIG. 10

The pyknometer should be just clear of the surface of the liquid when it is boiling.

When the liquid in the flask boils, the liquid in the pyknometer expands, carrying with it the last traces of air, until it has assumed the constant temperature equal to the boiling-point of the liquid.

The boiling is then stopped, and the pyknometer allowed to cool.

It is then taken out, dried, and weighed.

Calculation—

$$W_{\theta} = [(\text{pyk.} + \text{liq.}) - (\text{pyk.} + \text{air})]$$

$$V_{\theta} = \text{volume of pyknometer at } \theta^{\circ} \text{ C,}$$

where θ = boiling-point of the liquid.

14 DENSITY OF GASES, LIQUIDS, AND VAPOURS

Then the specific gravity will be—

$$\Delta_{\theta} = \frac{W_{\theta}}{V_{\theta}}.$$

Therefore the molecular volume—

$$V_m = \frac{m}{\Delta_{\theta}} = \frac{m \cdot V_{\theta}}{W_{\theta}},$$

where m is the molecular weight of the substance.

CHAPTER III

DETERMINATION OF VISCOSITY AND SURFACE TENSION

Viscosity—When a liquid flows through a tube, the velocity of the various portions of the liquid differ according as the liquid is in contact with the walls of the tube or not. That which is in contact with the walls of the tube moves very slowly, and for all practical purposes may be considered to be at rest. The next layer moves with a slightly greater velocity, and so on, the liquid at the axis of the tube having the greatest velocity. Thus we get a sheaving or movement of the layers one over the other. The relative velocity, therefore, of any consecutive layers will depend upon the *internal friction* or *viscosity* of the liquid. For the same tube, therefore, the velocity of the respective layers will *increase* more rapidly from the walls of the tube to the axis the *smaller* the *viscosity* of the liquid. The volume of liquid which under defined conditions flows through a given tube will depend on the viscosity of the liquid.

It may be shown that for the flow of a homogeneous liquid through a capillary tube that—

$$V = \frac{\pi p t}{8 \eta l} R^4.$$

or

$$\eta = \frac{\pi \cdot p t}{8 v l} R^4.$$

Where t in seconds is the time required for the volume V of the liquid to flow through a tube of length l ; R is the radius of the tube; p is the driving power, force, or excess of static pressure; η is the co-efficient of viscosity of the liquid. The assumption is made that the velocity of the liquid on leaving

the tube is zero. As this is not the case, however, it is necessary to make a correction for the kinetic energy of the liquid. For all practical purposes this correction may be omitted.

Determination of the Viscosity of Liquids: Method I—A simple apparatus for the determination of the viscosity of a liquid is as indicated in Fig. 11. An inverted bell-jar, fitted with a rubber stopper, through which passes a bent tube, which in turn is connected with a capillary tube of known

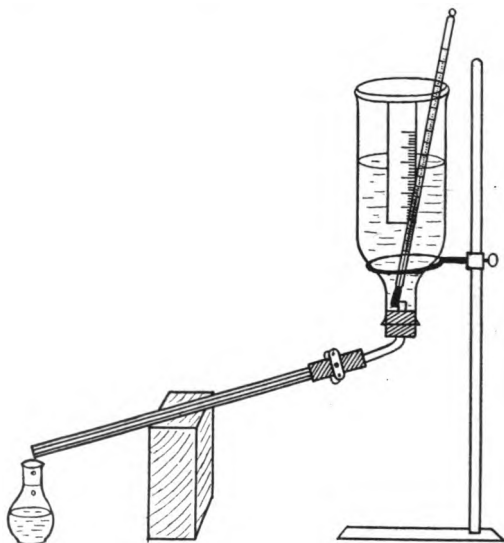


FIG. 11

bore. A scale is gummed on to the side of the bell-jar, so that the height of the liquid before and after the experiment may be noted. A small flask with a graduation mark on the neck is also required. Fill to a convenient level the bell-jar with the liquid to be tested, closing the exit by means of a pinch-cock on the rubber connection. Note the temperature of the liquid. Then open the pinch-cock, and allow the liquid to run out into the beaker to a definite mark on the bell-jar scale. At that instant replace the beaker by the graduated flask, and note the time (in seconds) taken to fill the flask up

to the graduation mark. When this point is reached, close the pinch-cock, and again note the level of the liquid in the bell-jar.

To determine the mean static pressure, p , measure the height of the two marks on the bell-jar scale, and subtract the height of the centre of the bore of the outlet tube; then $p = h\rho g$, where h is the mean height, g gravity acceleration, and ρ is the density of the liquid.

For actual calculation see next experiment.

Method II—A simpler and more convenient method is by using Ostwald's modification of Poiseuille's apparatus (Fig. 12). It consists essentially of a definite volume bulb, $a-b$, to which is attached a fine capillary tube, through which the known volume of liquid is allowed to flow, the mean driving-force being equal to the mean static pressure due to the difference in the level in the two limbs of the tube.

Introduce into " c " a definite volume of the liquid to be tested by means of an accurate pipette. Carefully support the apparatus in a thermostat with transparent sides (a large beaker fitted with a thermo-regulator will do).

When the apparatus has attained the temperature of the bath, adjust the level of the liquid to mark " a " by sucking through " e "; then close the tap e ; then open tap e , and carefully note the time with a stop-watch for the liquid meniscus to move from a to b . This should be repeated four or five times, and the mean result taken. The viscosity varies considerably with temperature; it is therefore essential that the temperature should be kept constant to at least 0.1° during a series of experiments. A suitable temperature to work is 25°C . A suitable exercise is the determination of the viscosity of benzene relative to water. The influence of temperature on viscosity is determined approximately by repeating the experiment at intervals, say, of 5° between 25°C . and 50°C . and plotting the results, from which the temperature co-efficient $\frac{\Delta\eta}{\Delta t}$ for 5° can be calculated.

The absolute value in C.G.S. units of the viscosity co-efficient of water at 25°C . is 8.95×10^{-3}

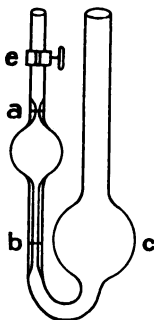


FIG. 12

Calculation—The force which drives the liquid through the capillary will be equal to $h\rho g$, where h is the *mean* difference of level of the liquid in the two limbs of the tube, ρ is the density of the liquid, and g gravity acceleration.

Now, if the experiment is repeated with a second liquid, we get the “driving force” in this case $h\rho_1 g$, from which we see that the driving force is proportional to the densities of the liquids, since h and g are constants.

The “co-efficients of viscosity” —

$$\eta = \frac{\pi p t}{8 v l} R^4 ;$$

therefore η for the same apparatus is proportional to the driving force p .

Hence we get—

$$\frac{\eta_2}{\eta_1} = \frac{h g \rho_2 t_2}{h g \rho_1 t_1} = \frac{\rho_2 t_2}{\rho_1 t_1}.$$

This gives the viscosity of the second relative to the first, which is all that is usually required. Water is usually taken as the comparison liquid. The co-efficient in absolute units may be calculated by substituting the absolute values in the equation for η .

Surface Tension—*Capillarity*—If a clean glass tube of fine bore is dipped into water, the water rises inside the tube. This elevation is due to the angle of contact between the glass and water being less than 90° , so that the surface tension tends to raise the water near the glass.

The resolved part of the force parallel to the axis of the tube is $2\pi r \sigma \cos \alpha$ where r is the radius of the tube, σ the surface tension, and α the angle of contact.

Now, the weight of liquid up the tube must be equal to this resolved force, and this latter is equal to $\pi r^2 h \rho g$, h being the height in the tube, and ρ the density of the liquid.

$$\therefore 2\pi r \sigma \cos \alpha = \pi r^2 h \rho g.$$

Now, $\cos \alpha$ is usually taken as 1 in cases where the liquids wet the glass:

$$\therefore \sigma = \frac{r \rho g h}{2}.$$

The value of σ is dependent on the nature of the liquid and also on the temperature.

Now, the molecular surface of different liquids will contain the same number of molecules, hence the product of the surface tension and the molecular surface of different liquids should be comparable quantities.

Now the molecular surfaces are proportional to $V^{\frac{1}{3}}$ where V is the molecular volume; therefore $\sigma V^{\frac{1}{3}}$ represents the *molecular surface energy*, or substituting Mv for V where M is the molecular weight of the substance and v is the specific volume, we get $\sigma Mv^{\frac{1}{3}}$.

Now, $\sigma(Mv)^{\frac{1}{3}}$ is a linear function of the temperature—

$$\sigma(Mv)^{\frac{1}{3}} = K(T_k - T),$$

where T_k is the critical temperature.

Therefore at temperatures T_1 and T_2 —

$$\sigma_1(Mv_1)^{\frac{1}{3}} = K(T_k - T_1),$$

$$\sigma_2(Mv_2)^{\frac{1}{3}} = K(T_k - T_2).$$

$$\therefore \sigma_1(Mv_1)^{\frac{1}{3}} - \sigma_2(Mv_2)^{\frac{1}{3}} = K(T_2 - T_1).$$

$$\therefore \frac{\sigma_1(Mv_1)^{\frac{1}{3}} - \sigma_2(Mv_2)^{\frac{1}{3}}}{T_2 - T_1} = K.$$

The value of K is the same for different liquids with certain exceptions, and has a value 2.12.

In certain cases, particularly when the liquid contains hydroxyl groups, the value obtained for K is less than 2.12. If, however, the molecular weight is multiplied by a factor x greater than one, the value 2.12 can be obtained.

The factor x is termed the *association factor*, and represents the number of times the mean molecular weight of the liquid is greater than the normal molecular weight.

Determination of Surface Tension of Benzene — Fit up apparatus as indicated in Fig. 13, which consists of a boiling-tube with side arm, fitted with a tight rubber stopper, through which passes a stout capillary tube. A graduated scale is fixed on to the capillary tube.

Put some benzene into the boiling-tube, and place the whole

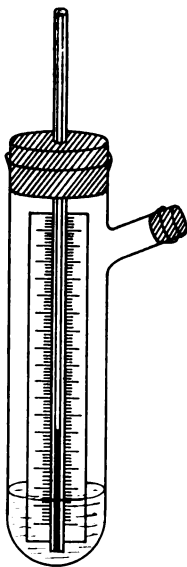


FIG. 13

into a thermostat at 25° C. When the apparatus has attained the temperature of the bath, blow slightly through the side tube so as to cause the benzene to rise up the capillary, and completely wet the sides. Then by means of a telescope read off the height of the benzene in the capillary tube. Three or four readings should be made, both after the benzene has been made to rise above (by blowing) and below (by sucking at the side tube) its final position.

Then from equation—

$$\sigma = \frac{r\rho gh}{2}.$$

The density of benzene at 25° C. may be taken as 0.8736.

r may be conveniently found by measuring carefully a thread of mercury in the capillary and then weighing it, and calculating r .

$$r = \sqrt{\frac{w}{\Delta\pi l}},$$

where w is the weight of the mercury, Δ the density of the mercury, and l the length of the thread.

From these data the surface tension can now be calculated.

To Determine the Molecular Surface Energy and Association Factor of Ethyl Alcohol—Repeat the above experiment with ethyl alcohol at 20° and 40°, and calculate, as before given. The density of alcohol at 20° = 0.7894, at 40° = 0.7722.

From which the molecular surface energy can be calculated thus :

$$\sigma = (Mv)^{\frac{1}{3}} \left(v \text{ specific volume} = \frac{1}{\text{density}} \right).$$

Now, for an associated liquid we have seen that—

$$\frac{\sigma_1(xMv_1)^{\frac{1}{3}} - \sigma_2(xMv_2)^{\frac{1}{3}}}{T_2 - T_1} = 2.12,$$

which on simplifying gives—

$$x = \left[\frac{2.12(T_2 - T_1)}{\sigma_1(Mv_1)^{\frac{1}{3}} - \sigma_2(Mv_2)^{\frac{1}{3}}} \right]^{\frac{1}{3}}.$$

Now, all terms except x are known, therefore the degree of association can be easily calculated.

CHAPTER IV

DETERMINATION OF SOLUBILITY

Solubility—When a solid is brought into contact with a liquid in which it is soluble, the solid continues to dissolve until a definite concentration is reached. The solid is then in equilibrium with the solution at the particular temperature of the experiment. When such conditions exist, the solution is said to be saturated. There are two methods usually employed for determining the solubility of solids in liquids.

1. Excess of the finely divided solid is shaken continuously with a definite quantity of solvent at a definite temperature until equilibrium is attained.

2. The solvent is heated with excess of the solute to a temperature slightly higher than that at which the solubility is to be determined, and then cooled to the desired temperature in contact with the solid.

Solubility curves are usually continuous so long as the solid phase or solid substance in contact with the solution remains unchanged. If, however, a change in the *solid phase* does occur, the solubility curve will show a *break*.

This is the case with sodium sulphate. The break is due to the fact that we are dealing with the solubility of two distinct substances, below 33° , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and above 33° , anhydrous (Na_2SO_4).

Experiment to Determine the Solubility of Sodium Sulphate—Take a stout glass tube, as indicated in Fig. 14, fitted with a stirrer. Introduce a quantity of finely powdered $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and fill the tube about two-thirds with distilled water. This should then be fixed in a thermostat and stirred for about two hours. Then allow the undissolved solid to settle, remove about 25 c.c. with a pipette, and carefully

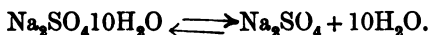


FIG. 14

evaporate to dryness on a water-bath, and thus determine the amount of solid dissolved in 25 c.c. of water. Then continue the stirring for another hour, taking care that some of the solid phase is always present, and again determine the amount of solid dissolved; repeat until constant results are obtained.

Repeat the above experiment every two degrees between 25° and 35°. Express the solubility in grams of anhydrous salt in 100 grams of water.

Plot your results graphically and determine the temperature of the break; this is the transition point of—



Experiment to Determine the Solubility Curve of Sodium Chloride up to 50° C.—The method is as in the previous experiment.

Experiment to Determine the Solubility Curve of Potassium Chloride up to 50° C.

Observe carefully the different characteristics of the three curves obtained from the above experiments.

CHAPTER V

DETERMINATION OF MOLECULAR WEIGHTS

IN the experiments about to be described it is necessary to use a thermometer which would be accurate to 0.002 of a degree. At the same time it is not usually necessary to know the exact temperature, but only changes in temperature.

For experiments of this type a Beckmann thermometer is used. It usually has a range of five or six degrees, and is graduated in tenths and hundredths. The thermometer is so constructed that the amount of mercury in the bulb can be to a certain extent controlled. This is rendered possible by having at the upper end of the capillary a reservoir, into which any excess of mercury can be driven, or from which further mercury can be drawn, as desired.

To set a Beckmann Thermometer—First invert the thermometer, and collect the mercury in the reservoir at the end which joins on to the capillary (see Fig. 15). Then carefully (so as not to dislodge the mercury in the reservoir) place the thermometer in a beaker of water; the actual temperature of the water is measured by an ordinary accurate thermometer, graduated at least in tenths. Now regulate the temperature of the bath until the column of mercury in the capillary joins completely the mercury in the reservoir. Then control the temperature of the bath until it is about two degrees above the highest temperature to be recorded in the actual experiment. Allow the thermometer to remain at this temperature for several minutes, and then strike the top of the thermometer sharply

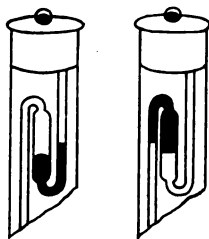


FIG. 15

with the palm of the hand, thus causing the mercury in the reservoir to fall, thereby becoming disconnected from the mercury in the capillary. Now allow the temperature of the bath to fall to the highest temperature to be reached in the actual experiment. If the setting has been successful, the mercury in the capillary should stand on the scale. If the mercury stands above the scale, there is too much mercury in the bulb; if too low on the scale, the mercury in the bulb is insufficient. In either case repeat the above operation, slightly raising or lowering the temperature of the bath at which the mercury column is separated from the reservoir, until the mercury stands at a convenient height on the scale at the highest temperature to be reached in the experiment.

Elevation of the Boiling-Point—When a non-volatile substance is dissolved in a liquid, the vapour pressure of the liquid is diminished; further, this diminution is proportional to the amount of solute added. Raoult, in 1887, after much experimental work, came to the following conclusions:

1. Equimolecular quantities of different substances, dissolved in equal volumes of the same solvent, lower the vapour pressure to the same extent.
2. The relative lowering of the vapour pressure is equal to the ratio of the number of molecules of solute, and the total number of molecules in solution.

A liquid boils when its vapour pressure is equal to that of the atmosphere. In the presence of a solute the difference between the vapour pressure of the solution and the atmosphere is greater than in the case of the pure solvent, hence in the case of a solution a slightly higher temperature is required than for the pure solvent to produce the slightly extra pressure.

It follows also that the elevation in temperature will be proportional to the lowering of the vapour pressure. Hence *Raoult's law may be re-interpreted thus: Equimolecular quantities of different solutes, in equal volumes of the same solvent, produce the same elevation of the boiling-point.* It is therefore possible to determine the molecular weight of any soluble substance by comparing its effect on the boiling-point of a solvent with that of a substance of known molecular weight.

If x grams of the substance of molecular weight m (where m is to be determined) be dissolved in W grams of solvent, raise the boiling-point by δ degrees, whilst m grams in

100 grams of solvent give a rise of K degrees, then we have—

$$\frac{x}{W} : \delta :: \frac{m}{100} : K.$$

$$\therefore m = \frac{Kx100}{W\delta}.$$

Van't Hoff has shown that K (which is termed the *molecular elevation constant*) can be calculated from the latent heat of vaporization of the solvent, and its boiling-point on the absolute scale :

$$K = \frac{0.02T^2}{H},$$

where T is the boiling-point, and H the latent heat of vaporization ; hence we get—

$$\begin{aligned} m &= \frac{100x}{W\delta} \cdot \frac{0.02T^2}{H} \\ &= \frac{2xT^2}{W\delta H}. \end{aligned}$$

Method I: Beckmann's Method—The apparatus, as is shown in Fig. 16, consists of a boiling-tube, A , to the side arm of which is attached a coiled condenser, K_1 , and through the upper stopper of which is introduced a Beckmann thermometer.

A stout bit of platinum wire is fused through the bottom of A , and a few glass beads are introduced to ensure uniform ebullition. This boiling-tube is surrounded by a jacket, B , which is made of glass (porcelain or copper for high temperatures), which is also fitted with a coiled condenser, K_2 .

The vapour jacket is supported by a small asbestos box, C , which is so constructed that the flames do not come directly under the boiling-tube A (see section). Two chimneys, S , carry the hot gases from the flames away from the apparatus. If the solvent boils below 60°C ., the coiled condensers should be replaced by small water condensers, which may be joined up in series. For hygroscopic solvents, calcium chloride tubes should be attached to the condensers.

Experiment to Determine the Molecular Weight of Camphor in Ethyl Alcohol—Weigh out carefully into the boiling-tube 15 grams of ethyl alcohol, introduce also a few clean dry glass

beads. See that bulb of the thermometer is just below the surface of the liquid. Introduce into the outer jacket a convenient quantity of alcohol (containing a little water, or a few drops of higher boiling liquid). Put in also one or two pieces of

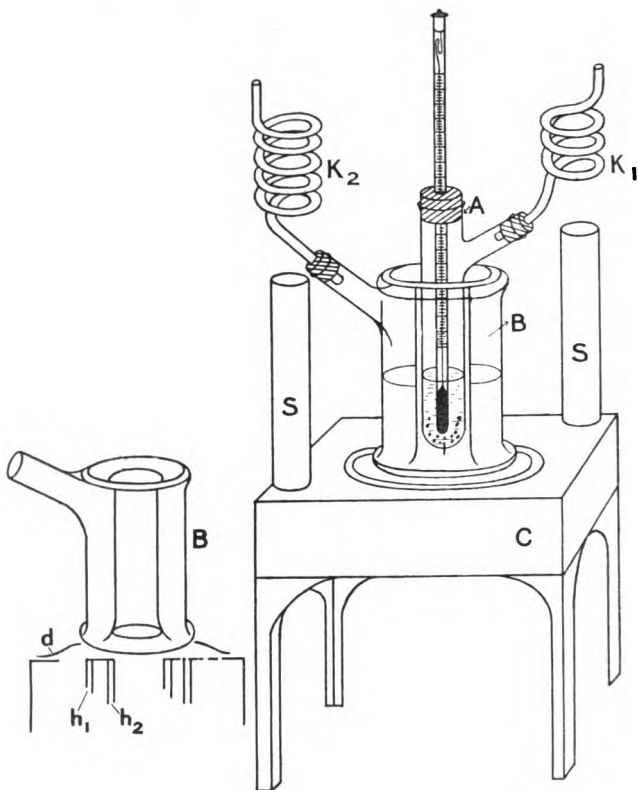


FIG. 16

porous tile. Then bring the liquid in the outer jacket to a steady boil, this will eventually cause the pure alcohol in *A* to boil. When the Beckmann reading has remained steady for at least five minutes, note the reading, and allow the apparatus to cool down ; and then introduce into *A* a small tabloid of camphor

(about 0.5 gram) accurately weighed. Now bring the liquid to boiling again, and when the reading on the thermometer is constant, note the temperature. It is essential that the rate of boiling should be as near equal as possible in both cases; this may be judged by noting the rate at which the drops fall back from the condenser attached to *A*. The thermometer should also be tapped before each reading, as the mercury column is very liable to stick. The barometric height should also be taken at each reading, and corrections applied, if necessary. Repeat the experiment, using 0.75 gram of camphor. Latent heat of vaporization of ethyl alcohol is 216.5 cals.,

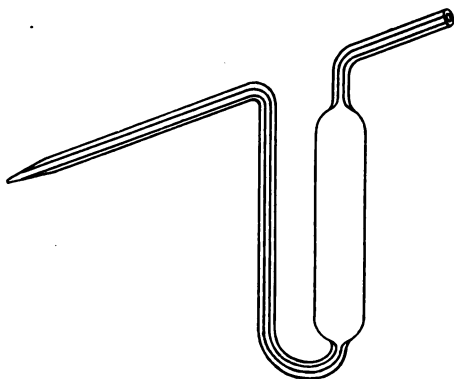


FIG. 17

B.P. 78.4° ; benzene may be used instead of ethyl alcohol as a solvent.

Experiment to Determine the Molecular Weight of Ethyl Benzoate in Benzene—In this case the liquid is introduced by means of a special pipette (see Fig. 17). The pipette containing the ethyl benzoate is first accurately weighed, and then a quantity introduced into the apparatus, and then weighed again. The loss represents the amount of solute used. Latent heat of vaporization of benzene, 93 cals., B.P. 80° .

Method II: Electrical Heating—A modified and much more convenient form of apparatus is indicated in Fig. 18. It consists of a boiling-tube fitted into a Dewar flask. Two narrow tubes, *t, t*, pass through cork, *W*, through the lower end

of each is sealed a piece of fairly stout platinum wire, and from these two wires is suspended the heating-coil.

The coil consists essentially of a glass spiral, which is broken in the middle at *M*. Through this spiral is threaded fine platinum wire (about 0.25 mm. diameter). The two ends of this wire are then fastened to the two stout wires, so that the coil hangs vertically, and also symmetrically with respect to

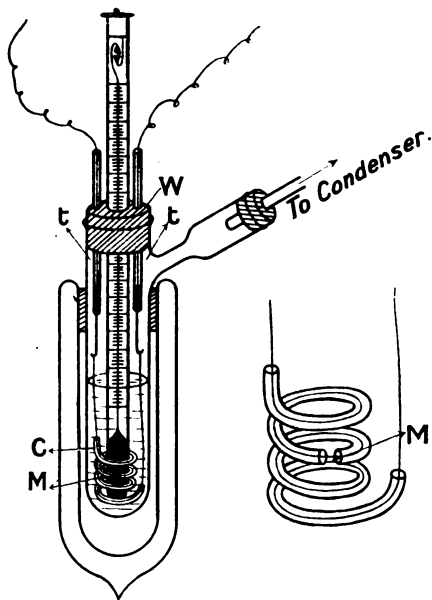


FIG. 18

the thermometer. A quantity of mercury is introduced into the tubes *t, t*, so that by means of copper wires inserted into the open end, so as to touch the mercury, the heating-coil may be connected with the source of electricity. A current from four or five accumulators, giving a current of 6 to 8 ampères, will usually be sufficient.

By having a glass spiral surrounding the wire the bulk of the liquid is eventually heated by its own vapour as it vaporizes within the spiral. In order to prevent superheating

it is essential to see the bubbles are issuing from the opening in the middle *M* and at the bottom. If bubbles come only from the middle and top, superheating is very probably taking place; this can be remedied by tapping the apparatus. The experiment described under Method I may be carried out with this apparatus in a similar manner.

Landsberger's Method—In this method the solution is brought to boiling-point by passing into it the vapour of the solvent. In

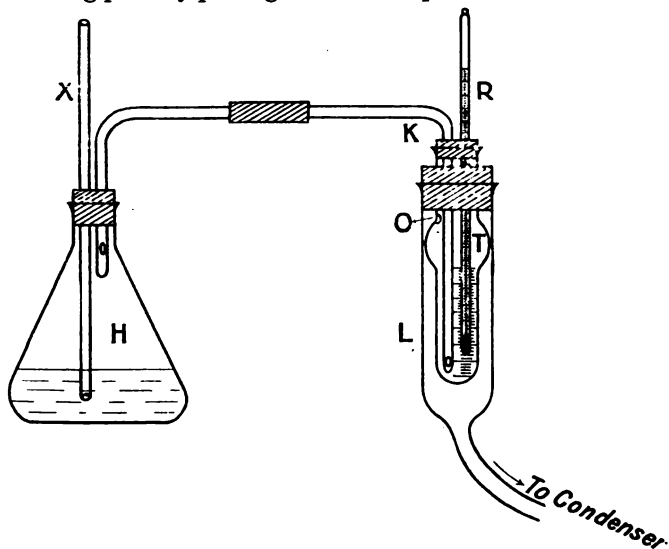


FIG. 19

this case there can be no fear of superheating, as the temperature of the vapour is lower than that of the boiling solution. The apparatus consists essentially of a graduated tube, *T*, with a small outlet at *O*. This tube is surrounded by a wider tube, *L*, which has a tube at the bottom to lead the vapours to a condenser. The thermometer *R* should be graduated in tenths. The pure solvent is boiled in flask *H*, from which the vapour is led into *T* by tube *K*. The tube *X* is merely a safety valve.

Experiment—Fit up the apparatus as shown in Fig. 19. Introduce into *H* a quantity of pure alcohol (also a few pieces

of porous tile). Place about 10 c.c. of alcohol in *T*. Boil the alcohol in *H*, and pass the vapour into the alcohol in *T*. Regulate the heating of the liquid in *H* so that when the alcohol boils in *T* the condensed vapour issues from the condenser at about one drop in two seconds. When the temperature is constant, read off the boiling-point of the solvent. Remove some of the solvent which has accumulated in *T* until about 6 or 7 c.c. remain. Fill up, if necessary, flask *H*. Now introduce into *T* a small tabloid of camphor, and repeat the above process, taking care that the rate at which the solvent issues from the condenser is similar to that in the previous case. Note the temperature when practically constant. Then turn out the flame under the boiler, and *rapidly* disconnect from the rest of the apparatus. Then read off accurately the volume of liquid in *T* to a tenth of a centimetre. Reconnect with the boiler, and repeat the experiment three times. On each occasion the volume of solution in *T* will change, but for each volume there will be a corresponding temperature; for in each case the concentration of the solute will be different, hence the change in the boiling-point.

Note—It is advisable to renew the porous tile in *H* after each disconnection.

Calculation—In this the equation will be—

$$m = \frac{Kx100}{VS\delta},$$

where *V* is the volume read off, and *S* the density of alcohol at the temperature at which the reading is made (boiling-point). The ratio $\frac{K}{S}$ is sometimes known as the constant of Landsberger's method.

Hence, if we put $C = \frac{K}{S}$, we get—

$$m = \frac{Cx100}{V\delta}.$$

C for alcohol = 15.6.

Compare the results obtained by this method with those obtained by Beckmann's method.

Experiment to Determine the Molecular Weight of Benzoic Acid in Ether by the Method described above :

Depression of the Freezing-Point—Where possible, this method is used in preference to the boiling method, because much more accurate determinations can be made.

The apparatus is due to Beckmann, and is as shown in Fig. 20. The inner tube *A*, which is provided with a thermometer and stirrer, and also a side tube, contains the solvent, the freezing-point of which is to be determined.

A is fastened to the wider tube *B* by means of a cork, which is in turn supported by a metallic cover in the bath *C*, in which the freezing mixture is placed. The vessel *C* is provided with a stirrer and also vessel *A*; in the latter case it should be of platinum, but, without any serious error it may be of glass. The depression in freezing-point is determined by means of a Beckmann thermometer, which is fitted by means of a cork in *A*. Between *B* and *A* is an air mantle, which controls the fall in temperature by causing the solvent to cool gradually. In carrying out an experiment the temperature of the freezing mixture should not be more than 3° or 4° below the freezing-point of the solvent, and, further, the temperature of the bath should be kept as constant as possible.

Method — In an experiment about 20 grams of solvent are introduced into *A*; stir the solvent uniformly (not too vigorously), and from time to time stir the freezing-bath. Owing to the supercooling this temperature falls below the freezing-point of the solvent, but as soon as any solid begins to separate out the temperature rises again, owing to the evolution of the latent heat of fusion of the solvent. The amount of supercooling can be reduced by the introduction of a crystal of solvent as soon as the temperature falls below the

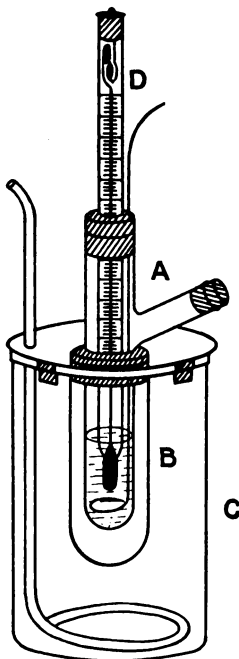


FIG. 20

freezing-point. The highest temperature observed after the formation of solid is taken as the freezing-point, because the temperature cannot rise naturally above the melting-point of the solid while solid is still present. (A slight error is introduced due to the friction of the stirrer in *A*, and also conduction from outside by stirrer, thermometer, etc., but this need not be considered here.) *A* is now removed and accurately weighed, a quantity of the solute added, and the determination of the freezing-point repeated. If the temperature of the freezing-bath has also been carefully adjusted, the solvent will separate out slowly, and the highest temperature reached soon after the formation of a little solid is taken as the freezing-point. If, however, the temperature of the bath is too low, or there is considerable supercooling, the separation of solid solvent will be too great, and the temperature of this equilibrium will be that of a much more concentrated solution than that originally prepared, and the more concentrated the solution, the greater is the depression produced.

Calculation—The calculation is made by a similar method to that used in the case of boiling-point determinations.

$$\frac{Kx100}{W\Delta} = m,$$

where Δ is the depression.

$$K, \text{ as before, } = \frac{0.02T^2}{H}.$$

Experiment to Determine the Molecular Weight of Acetone in Acetic Acid—Introduce into *A* 25 grams of pure glacial acetic acid. Use as a bath water at about 12° to 13°. Determine the freezing-point as described above. Now introduce by means of a pipette (see Fig. 17) about 0.5 gram of acetone (determine weight by difference), and redetermine the freezing-point.

Experiment to Determine the Molecular Weight of Naphthalene in Benzene—Use a bath of ice and water giving a temperature of about 2° C. Where the temperature of the solvent is a fair way off its freezing-point, preliminary cooling may be done by immersing tube *A* directly in the freezing-bath until the solvent is within 1° or 2° of its freezing-point. Use 0.25 gram of naphthalene in 25 grams of solvent.

Abnormal Molecular Weights—It frequently happens the molecular weights obtained by the above method do not agree with those obtained by other methods. They are in some cases greater and in other cases less. Now, the depression of the freezing-point is proportionate to the number of molecules dissolved in a given volume of solvent. Hence the only conclusion is that the number of molecules in solution is greater or less than it should be—*i.e.*, *dissociation or association* has taken place. Consider the case of *association*: Let x be the degree of association, then $1 - x$ represents the unassociated molecules. If n represents the complexity of the associated molecules, then $\frac{x}{n}$ will represent the number of associated molecules. Hence in a molecular solution the number of molecules will have been reduced in the ratio $1 : 1 - x + \frac{x}{n}$. Therefore the decrease of the observed depression from the theoretical depression will be in the ratio of—

$$\frac{1 - x + \frac{x}{n}}{1}$$

i.e.,

$$\frac{\Delta_o}{\Delta_t} = \frac{1 - x + \frac{x}{n}}{1},$$

where Δ_o is the observed depression, and Δ_t the calculated depression. Hence—

$$x = \frac{\Delta_t - \Delta_o}{\Delta_t \left(1 - \frac{1}{n}\right)},$$

or since

$$\frac{M_t}{M_o} = \frac{\Delta_o}{\Delta_t},$$

we get

$$\frac{M_o - M_t}{M_o \left(1 - \frac{1}{n}\right)}.$$

If dissociation takes place, the equation becomes—

$$x = \frac{\Delta_o - \Delta_t}{\Delta_t(n-1)},$$

or

$$x = \frac{M_t - M_o}{M_o(n-1)}.$$

By applying the above, the degree of *association* or *dissociation* of a solute may be determined.

Suppose in equation—

$$m = \frac{Kx100}{W\Delta} \quad . \quad . \quad . \quad . \quad (1)$$

we assume m from other sources and calculate K , and compare it with the value obtained from Van't Hoff's equation—

$$K = \frac{0.02T^2}{H} \quad . \quad . \quad . \quad . \quad (2)$$

If association has taken place, K will be less ; if dissociation, greater in equation (1) than in equation (2).

Example K for cane sugar in water is 18.6, for sodium chloride in water 36.0, for methyl iodide in benzene 50.4, for benzoic acid in benzene 25.4. The normal values are 18.6 and 51.2 in water and benzene respectively.

Note—One value of K is approximately double the other for each solvent.

Experiment to Determine the Apparent Molecular Weight of Potassium Chloride in Water, and from the Result Calculate the Degree of Ionization—Carry the determination as in previous experiment. Introduce a crystal of ice to prevent excessive supercooling.

CHAPTER VI

DETERMINATION OF TRANSITION POINTS

MANY substances are capable of existing in two or more crystallized forms, but the various forms are not equally stable under the same conditions.

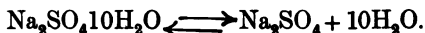
Sulphur is one of the best known examples. Rhombic sulphur is stable at ordinary temperatures, and on heating melts at 115°C . On being kept for a time at about 100°C . it changes completely into the monoclinic variety, which has a melting-point of 120° . Monoclinic sulphur can be kept for an indefinite period at temperatures, say, 100° to 110°C . without undergoing any further change. Rhombic sulphur however, changes to monoclinic at these temperatures. Monoclinic sulphur is therefore the stable form under these conditions. Thus there is a temperature above which monoclinic sulphur is the stable form, and below which rhombic sulphur is the stable form, and at which the two forms are in equilibrium with their vapour—i.e., a temperature at which neither form changes into the other on keeping. This temperature is termed the *transition temperature*, or *transition point*, and is in the case of sulphur 95.6°C .

When a salt combines with water to form more than one hydrate, it is found that only one hydrate is stable under any given conditions of temperature, etc., or conditions may arise when the anhydrous salt is the stable variety. Thus, we find transition points in the case of salt hydrates, that is to say, on passing a certain temperature the composition of the salt hydrate changes to another definite composition, while at this temperature the two definite hydrates (or anhydrous salt) can co-exist.

Thus on heating sodium sulphate decahydrate to a temperature above 33°C . it is found that decomposition occurs into

anhydrous sodium sulphate and a saturated solution of the *anhydrous salt*.

If, on the other hand, a saturated solution of sodium sulphate, at say 40° C., in presence of an anhydrous salt, be allowed to cool, when the temperature has fallen below 33° C. the anhydrous salt takes up water and forms decahydrate crystals. 33° is therefore approximately the transition-point for the change.



Determination of the Transition-Point—(1) Thermometric Method—When one system changes into another, the change is almost invariably accompanied by some heat effect, either absorption or evolution of heat. Thus, on heating, say $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the temperature rises normally until the decahydrate begins to change into the anhydrous form; at this point the temperature remains practically stationary until the transformation is complete, since heat is absorbed by this change. Hence, by noting the temperature at which this retardation occurs, the transition-point may be determined. When the reverse change is allowed to take place, there is an evolution of heat.

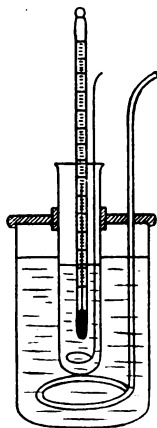


FIG. 21

In actual experiment it is usual to plot both the heating and cooling curves.

Experiment to Determine the Transition-Point of Sodium Sulphate—Take about 40 grams of pure sodium sulphate decahydrate in a thin glass boiling-tube. Hang a thermometer, which should be graduated in tenths of a degree, so that the bulb is completely surrounded by the decahydrate. Support the tube in a large beaker of water, which can be heated very gradually with a small flame. The temperature of the bath should be kept uniform by means of a stirrer (see Fig. 21). Raise the temperature of the bath to about 31° C., and then keep the temperature constant for a short time. Now very slowly raise the temperature until the salt becomes partially liquid. At this stage the salt should also be kept constantly stirred. The rate of rise in temperature at

this stage should not be more than about 1° in 10 minutes. When the salt has begun to liquify, the temperature should be read every minute. A point is reached at which the temperature is practically stationary for an interval. This is due to the *absorption* of heat during the transition from the decahydrate to the anhydrous salt and solution.

After a time the temperature begins to rise gradually again. When the temperature has reached about 36° C., allow to cool, stirring constantly, the bath and the salt. Again take readings every minute; a period of approximate constancy will be noted, in this case due to the *evolution* of heat, owing to the reformation of the decahydrate. Now plot these temperature readings against time, and draw the two curves, one for rising temperature and the other for falling temperature. Theoretically one would expect these two curves to be identical. They are both of the same type, but the vertical portions do not coincide.

This lack of coincidence of the two curves is due to what is termed *suspended transformation*. At the higher temperature we are dealing with a solution of the anhydrous salt, and after passing below the transition-point, it is possible for the solution of the anhydrous salt to exist, if the *stable phase*, in this case the decahydrate, is entirely absent. Such a solution is, however, unstable. The amount of *lag* can be considerably reduced by vigorous stirring in the neighbourhood of the transition-point.

The amount of *lag* can also be reduced by allowing the temperature to change very slowly in the neighbourhood of the transition-point.

The general type of such curves is as indicated at Fig. 22.

(2) **Dilatrometric Method**—This method depends upon the fact that change from one system to another, on passing through the transition-point is accompanied by an appreciable change in volume, and it is only necessary to determine the temperature at which this change of volume occurs in order to ascertain the transition-point. This variation in volume is studied by means of a *dilatometer*, which consists of a long capillary tube about 0.5 mm. internal diameter, to which is attached a long bulb (Fig. 23).

Experiment to Determine the Temperature of Formation of Astracanite from the Simple Salts—Take equimolecular weights of sodium sulphate decahydrate, and magnesium sulphate hepta-

hydrate; powder each up, and mix them by stirring with a glass rod. Protect the capillary tube by a small glass bead,

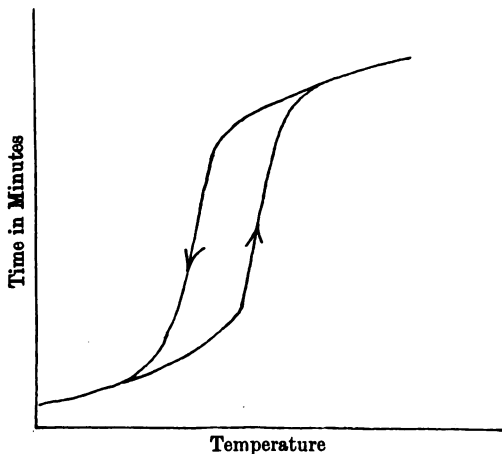


FIG. 22



FIG. 23

and then introduce some of the mixture into the bulb, filling it about three-quarters full; then seal off the open end of the bulb; invert and shake the solid mixture down to the bottom of the bulb. It now remains to fill the rest of the bulb and part of the capillary with some suitable liquid. To do this fix an adapter to the capillary (as shown in Fig. 24), and introduce a quantity of xylene. Attach the adapter to a water-pump and exhaust the dilatometer, then, on suddenly admitting the air, the xylene will be driven down into the bulb. This operation is repeated until all the air has been removed. It is necessary to tap the tube to remove any air which is entrained in the solid mixture. Fix some suitable scale to the capillary, and adjust the meniscus by pushing a piece of thin platinum wire down the capillary, and thus driving out some of the xylene. Immerse the bulb of the

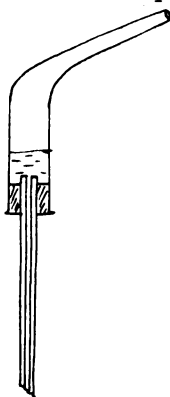


FIG. 24

dilatometer in a beaker of water at 16°C ., and note the height of the meniscus. Raise the temperature 1° at a time, and take reading of the height of the meniscus, each degree each time waiting until the meniscus has come to rest; continue up to 25°C . Now allow the bath to cool, and again take readings every degree, and so obtain a cooling curve. Plot the results obtained—*i.e.*, plot the heights of the meniscus as ordinates against temperature readings. An abrupt increase in volume will be noted about 21° to 22° on the heating curve, and an abrupt contraction on the cooling curve at about the same temperature. The two curves, however, do not coincide, the expansion taking place at a slightly higher temperature, and the contraction at a slightly lower temperature, than the true transition-point. The curves are very similar to those obtained in the previous experiment.

(3) Vapour Pressure Method

—When one system can be transformed into another, the vapour pressures of the two systems are identical at the transition-point. This method has, so far, only been applied to systems containing water or other volatile component. For the purpose of making these measurements a differential manometer is used. The most convenient form is known as Bremer-Frowein tensimeter, which is as shown in Fig. 25. It consists of a U tube, the limbs of which are bent close together, and backed by a millimetre scale. The bend is filled with oil, or bromnaphthalene, or some other suitable liquid.

The substances the vapour pressures of which are to be compared are placed in the bulb *a, b*, and the necks then sealed off. The apparatus is then inclined so that the liquid in the bend

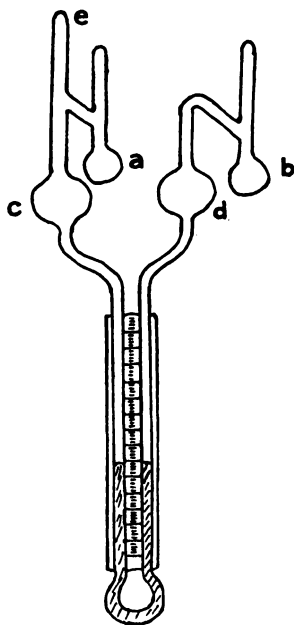


FIG. 25

collects in the bulbs *c*, *d*. The open end *e* is then connected to a mercury pump, and the apparatus completely evacuated. The tube *e* is then sealed off. The apparatus is then placed perpendicularly in a thermostat, and the differences in level read.

Experiment to Determine the Transition of Sodium Sulphate— In this case fill the bend of the tube with bromnaphthalene, and into the bulbs *a*, *b* respectively introduce pure dry powdered crystals of the decahydrate, and crystals moistened with a little water so as to make a saturated solution. Exhaust the apparatus and seal off as previously indicated, and place the tensimeter perpendicularly in the thermostat at 25° C., allow the difference in pressure to become constant, and then read it off. Then slowly, as before, raise the temperature, noting each degree the difference in pressure. At the transition-point the vapour pressure of the crystals of decahydrate must become equal to that of a solution saturated with the decahydrate and anhydrous salt.

(4) **Solubility Method**—The transition-point of Glauber salts may be determined by plotting the solubility for the anhydrous salt and the decahydrate respectively. The point of intersection of the two curves gives the transition-point. The experimental details of this method are indicated in the chapter on Solubility.

CHAPTER VII

OSMOTIC PRESSURE

WHEN a dilute solution of a substance in water is placed in a vessel closed with an animal membrane, such as a bladder, and the whole immersed in water to a depth that the level of the water outside is the same as the level of the solution inside, it is observed that the volume of the liquid in the inner vessel increases, and this is made manifest by the rise of the liquid in the vessel. It is obvious from this experiment that water must have passed from the outer vessel through the membrane to the inner vessel. But if the outside liquid is examined, a quantity of solute will be found to be present. Hence some of the solution must have found its way through the membrane. After the solution has risen to a certain height in the vessel, the liquid begins to fall gradually, due to the fact that the solutions continues to penetrate the membrane.

Many attempts were made to find some general relationship between the height the liquid rose in the vessel and the concentration of the solution. But at first this was found impossible, since the amount of solution which escaped varied with different membranes. Later, however, it was discovered (Traube 1867, Pfeffer 1877) that artificial membranes could be prepared which, while allowing the passage of water through them just as in the case of animal membranes, unlike these materials, they offered a perfect barrier to the passage of many substances in solution in the water. If a solution of copper sulphate is brought very carefully in contact with a solution of potassium ferrocyanide, a delicate film of copper ferrocyanide forms where the two liquids come into contact. The student can see this very effectively by performing the following experiment.

Experiment—Let a drop of a cold saturated potassium ferrocyanide solution run from a fine glass capillary into a 0.5 molar solution of copper sulphate contained in a glass vessel. Detach the drop by a slight motion of the tube so that it sinks to the bottom of the vessel. The drop at the moment of its entrance into the solution became surrounded with a thin film of cupric ferrocyanide, which keeps growing in thickness at the expense of the dissolved components. The concentration of the solute within the membrane is greater than that of the copper sulphate outside, hence water passes into the globule and the membrane expands, because of the pressure caused by the entrance of the water through the walls. The membrane is at first transparent and traversed by brown veins. As the expansion of the cell continues, the specific gravity of the contents diminishes until it becomes less than the copper sulphate solution; then the cell rises to the surface of the solution. In time, however, the walls become sufficiently thick to cause the cell once more to sink to the bottom, where it remains permanently.

The copper ferrocyanide film, however, is very delicate, and, to be of any practical value, has to be supported. This is most conveniently done by precipitating the copper ferrocyanide within the walls of an unglazed porcelain vessel. By this means an area of film which can be utilized is obtained. In reality it is built up of a very large number of very small films, each of which is supported by the porcelain particles round it. The membrane thus obtained is *almost* completely unpermeable to a great many solutions, and for our purpose be regarded as a true semipermeable membrane.

Preparation of a Semipermeable Membrane—Take an unglazed porcelain pot 8 or 10 cms. high and 2 to $\frac{3}{4}$ cms. diameter. Soak it in water for several hours, then fill up the pot to near the top with a solution of copper sulphate containing 2.5 grams per litre, immerse this in a beaker containing a solution of potassium ferrocyanide of a strength 2.1 grams per litre, so that the levels of the liquid, both inside and outside the pot, are about equal. Allow to stand for several hours. The salts diffuse through the walls, and where they meet a copper ferrocyanide membrane is formed, which, since it is impermeable to the salts from which it is formed remains quite thin, but is capable of withstanding fairly large pressures since it is supported by the walls of the porous pot. The porous pot is then taken out and thoroughly washed.

Experimental Determination of Osmotic Pressure—A suitable form of apparatus is shown in Fig. 26. A tube *B*, of such a diameter that as near as possible it just fits inside the porous pot, is fixed to the porous pot by surrounding the junction with a glass collar, *C*, the whole being held in position by filling the surrounding space with cement or sealing-wax, the joint being perfectly air-tight. The top of the tube *B* is closed by a stopper, through which passes a glass tube *E*, which is drawn out at the end. To the side tube *F* is attached a graduated manometer, provided with a reservoir bulb, *H*.

Experimental Determination of the Osmotic Pressure of Cane Sugar Solution—Fit up the apparatus as previously described. Prepare a 1 per cent. solution of cane sugar, and fill up the porous pot to near the top by removing cork *E*.

Then attach the manometer and make joints *E* and *F* perfectly air-tight by coating the junctions of the stoppers with the glass with a layer of some suitable cement or sealing-wax. The tube *E* has up to now been open to the air, thus preserving atmospheric pressure throughout the apparatus until all joints were tight—i.e., the mercury in the manometer is the same in both limbs. Now seal off *E*

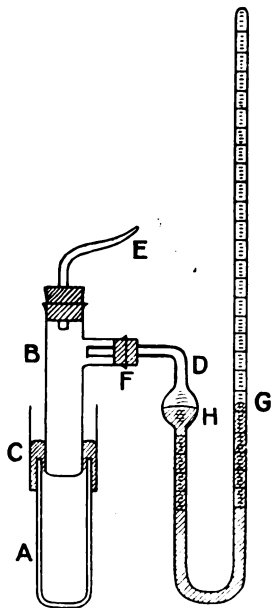


FIG. 26

in a blowpipe (note *E* has been already drawn out to a fine point, so that the sealing off is only a matter of a second or so), and note carefully the manometer reading. Now immerse the porous pot in a beaker of distilled water at room temperature. Water gradually passes into the cell, and the air in the upper part of the apparatus is compressed, and thus drives up the mercury in the manometer, thus measuring the pressure inside the cell. Take readings every hour, then allow to stand over night, and take readings again until no alteration occurs. The actual time required depends upon the particular cell. If the cell h

been well prepared, the maximum pressure will be retained for several days. Make a note of the maximum pressure. According to Pfeffer the osmotic pressure of a 1 per cent. solution of cane sugar is 535 mm. of mercury.

For higher concentrations the osmotic pressure of cane sugar solutions rises to considerably more than an atmosphere, and a manometer of the closed type has to be used—for example, a 6 per cent. solution of cane sugar has an osmotic pressure of 3075 mm. of mercury at room temperature.

Osmotic pressure measurements do not make suitable laboratory exercises, but students ought to be familiar with the method by performing the experiment described above. The apparatus once set up, other experiments may be done while equilibrium is being established. Where necessary, five or six students may take readings from one apparatus.

The following laws relating to osmotic pressure have been established :

1. Temperature and concentration being the same, different substances, when in solution, exert different pressures.

2. For one and the same substance, at constant temperature, the pressure exerted is proportional to the concentration.

3. The pressure for a solution of a given concentration is proportional to the *absolute* temperature, the volume being kept constant.

4. Equimolecular quantities of different substances, when dissolved in the same volume of solvent, exert equal pressures under the same conditions of temperature and pressure.

Note—This is only true of those substances whose molecules neither dissociate into simple forms (*i.e.*, non-electrolytes), nor associate into more complex molecules when in solution.

It will be observed that the second statement is analogous to Boyle's law ; the third corresponds to Charles's law ; while the last is an extension of Avagadro's hypothesis. Hence Van't Hoff came to the following conclusion :

"The osmotic pressure exerted by any substance in solution is the same as it would exert if present as a gas in the same volume as that occupied by the solution, provided that the solution is so dilute that the volume occupied by the solute is negligible in comparison with that occupied by the solvent."

EXAMPLES FROM PFEFFER'S RESULTS

Percentage of Sugar in Solution	Osmotic Pressure in Mm. of Mercury = P.	Volume of Solution containing 1 Gram of Sugar = V.	P. V.
1	535	C.c. 99.6	53286
2	1016	49.6	50394
4	2082	24.61	51238
6	3075	16.34	50245

CHAPTER VIII

REFRACTIVITY MEASUREMENTS

Refractive Index—When a ray of light passes from one medium to another, and the densities of the two mediums are different, the direction of the ray is altered, except when the ray is perpendicular to the boundary between the two media, in which case no change occurs. This latter position is called the *normal*. Consider

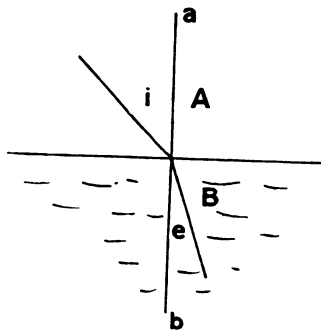


FIG. 27

Fig. 27. Let *A* and *B* represent the two media where *B* is denser than *A*, also let *a—b* represent the normal, then a ray of light passing through *A* at an angle “*i*” to *a—b* will be deflected on entering *B* in such a manner that angle

“*e*” is less than angle “*i*.” In other words the *angle of incidence*, “*i*,” will be greater than the *angle of refraction*, “*e*.”

The relation between these two angles is termed the *refractive index*, and further it can be shown that—

$$\frac{\sin i}{\sin e} = \frac{N}{n},$$

where *N* is the refractive index in the denser medium, and *n* the refractive index of the less dense medium.

It will be seen that the maximum value for *i* is 90°, in which case $\sin i = 1$; then—

$$\sin e = \frac{n}{N}.$$

Determination of the Refractive Index of a Liquid—The principle indicated above is used in determining the refractive index of a liquid, the index of refraction being found by comparison with a glass prism of known refractive index, which must be greater than that of the liquid.

In actual practice monochromatic light is used, since white light would give spectrum effects, thereby preventing the obtaining of sharp and definite images. Consider Fig. 28, which represents a glass cell containing the liquid to be examined, mounted on a right-angled glass prism of refractive

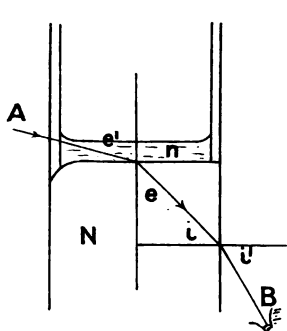


FIG. 28

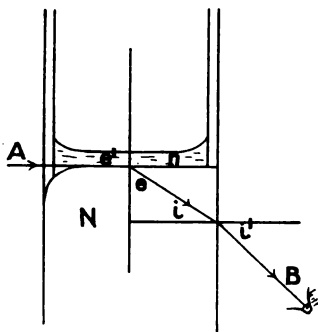


FIG. 29

index, N . Then a ray of light (Fig. 28) entering at A will have a path somewhat as indicated, and the relation $\frac{\sin e'}{\sin e} = \frac{N}{n}$ exists. Suppose now the angle e' is gradually increased: a point is reached when no light is visible at B , this occurs when angle e' becomes 90° . At this point the light is totally reflected. The ray of light is entering horizontally, as shown in Fig. 29, and in actual practice it is the position at which this occurs that is determined. Thus, when $e' = 90^\circ$ we have—

$$\sin e = \frac{n}{N}$$

n being the refractive index of the liquid, and N that of the glass prism.

Further,
$$N = \frac{\sin i}{\sin i'}$$

But
$$\sin e = \cos i;$$

$$\therefore \cos i = \frac{n}{N}$$

—i.e.,
$$n = \cos i N,$$

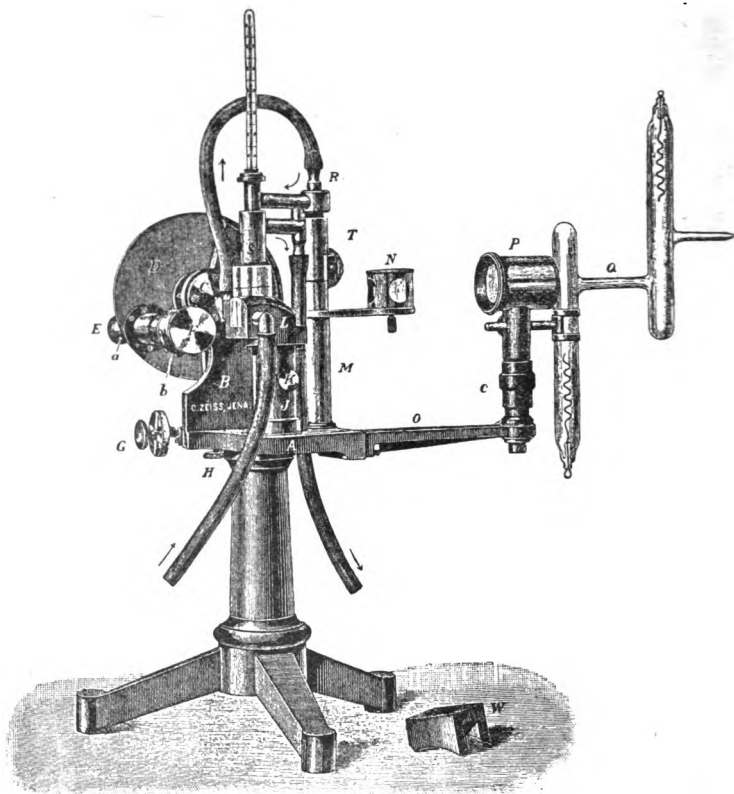


FIG. 30

But $\cos^2 i = 1 - \sin^2 i$;

$$\therefore n = N \sqrt{1 - \sin^2 i}.$$

Substituting $\frac{\sin^2 i'}{N^2}$ for $\sin^2 i$,

we get $n = \sqrt{N^2 - \sin^2 i'}.$

Hence we see that to find n we have to determine the value of i' when the incident ray is horizontal. In actual practice it is not usually necessary to go through the above calculation, since the makers supply tables giving values of n for each value of i' .

Specific and Molecular Refractivity—The refractive index varies with the temperature of the liquid, and according to Gladstone and Dale $\frac{n-1}{d} = \text{constant}$, where d is the density of the liquid; Lorentz and Lorenz, however, find the expression $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ gives a better constant. The value of this expression is termed the *specific refractivity* of the liquid. This value is dependent only on the *nature* of the liquid, and is a characteristic property of it.

Molecular Refractivity is found by multiplying this value by the molecular weight of the substance. $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d}$ gives a constant, where M is the molecular weight of the substance.

Method of Determination of the Refractive Index—The best instrument to use for this purpose is the *Pulfrich* refractometer, which is somewhat as shown in Fig. 30.

L is a refracting prism, on which is mounted a glass cell; this is clamped in position by the screw K , so that the flat face of the prism faces the telescope F . Since a constant temperature is required, the temperature of the liquid in the cell is controlled by heater S (see section, Fig. 31), through which water from a thermostat is circulated. A thermometer screwed into the heater indicates the actual temperature inside the cell. At the end of the telescope nearest to the prism is a cap, in which is an oblong slit, through which the light passes after refraction. With a single cell the whole slit is used, but with a divided cell half the slit is used.

Near the eyepiece end of the telescope is a large graduated metal disc, D , which is graduated in degrees and half-degrees. A vernier is also provided, by means of which a single minute can be read off. This vernier reading is made by the aid of a telescope, which can be rotated round the disc. To make the final adjustment the disc is fixed by screw H , and the fine adjustment made by means of screw G .

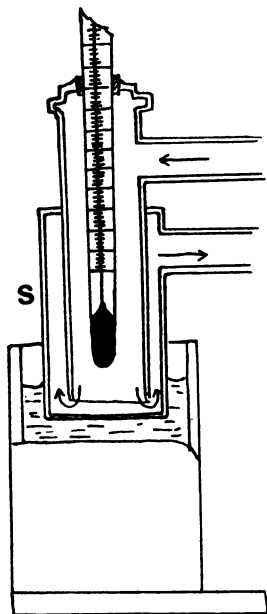


FIG. 31

N is a reflecting prism on a movable arm, and P is a lens by means of which the light can be focussed on to the centre of the cell. In any experiment it is essential that the ray of light should be monochromatic and of a definite wave length. There are three spectrum lines, which are generally used for this purpose. D line (given by sodium flame), C line (red line of the hydrogen spectrum), and the F line (the blue line of the hydrogen spectrum). The D line is obtained, say, from sodium chloride in a bunsen flame, C and F lines are obtained from Geisler tubes.

Determination of the Zero-Point

—A small right angle prism is let in the telescope tube near the eyepiece for the purpose of determining the zero of the instrument. This prism is illuminated by some strong source of light, such as an electric lamp. This light is reflected along the telescope. Here it emerges through the slit at the other end and strikes the face of the prism, thereby being reflected back along the telescope. Hence, on looking through the eyepiece, the small prism, and also an image of it, are seen on the right and left of the field of view respectively. On the image are seen two dark lines running parallel to the cross wires; these are the reflected images of the cross wires (see Fig. 32). Rotate the graduated disc until the cross wires and their images coincide as near as

possible. Tighten screw *H*, and make the final adjustment by means of screw *G*.

Now observe the vernier reading, and the difference of this from zero is the correction which has to be applied to every subsequent reading.

It sometimes happens that the simultaneous coincidence of the cross wires with their images cannot be obtained. In this case the true zero is obtained by taking the reading when the upper wire coincides with the upper image, and again when the lower wire coincides with the lower image, and then taking the mean of the two readings. The drum on the fine adjustment screw is divided into 200 divisions, and moves along a horizontal scale, which is divided into degrees and thirds of a degree. One complete turn of the drum corresponds to a third of a degree ($20'$), therefore one division on the drum is equal to $0.1'$.

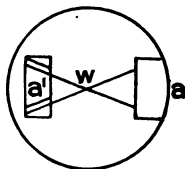


FIG. 32

Experimental Determination of the Refractive Index of Alcohol for D line—The sodium flame is placed about 2 feet from the reflecting prism *N*, which must be arranged so as to throw an image of the flame on the cell which is mounted on the refracting prism. Usually a wooden cap, *W*, with a side slit, is placed over the cell to exclude extraneous light; it also serves to keep the temperature constant.

Introduce a layer of alcohol about 5 mm. deep by means of a pipette, taking care not to touch the polished surface of the prism. Now bring into position the heater, lowering the movable flange until it is in contact with the top of the cell. Circulate the water from the thermostat at 25° C. through the heater, and when the temperature becomes constant to 0.1° , a measurement may be made.

Rotate the graduated disc until a bright yellow band crosses the field of view. Then clamp it by means of screw *H*, and then by means of screw *G* arrange the intersection of the cross wire on the upper edge of the yellow band. The reading then gives the angle of emergence, from which the index of refraction can be obtained from the tables.

The tables are usually divided into six columns; i' is the angle of immersion obtained as above, n_D is the value calculated from $n = \sqrt{N^2 - \sin^2 i'}$, Δ_n is the amount in units to be

subtracted from the *last* decimal place for a rise 1' in the value of i .

The last three columns are corrections when C, F, G lines are used. Having obtained the refractive index n , the *specific refractivity* can be calculated from the formula of either Gladstone and Dale $\frac{n-1}{d} = R$, where R is the specific refractivity, or that of Lorentz and Lorenz, in which case—

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{1}{d},$$

the value of d being obtained either from tables, or directly by the method given for the determination of the density of liquids.

The *molecular refractivity* will be—

$$MR = \left(\frac{n-1}{d} \right) M \text{ and } MR = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$$

respectively, where M is the molecular weight of the liquid.

It has been found from measurements on a large number of organic liquids that the molecular refraction may be represented as an approximate summation of the atomic refractivities, so that the refractive power is largely an additive property.

The values given for n in the tables are usually for a temperature of 20° C., so that if the experiment is done at 25°, it is necessary to make a correction. This correction will be found in another table.

CORRECTION FOR TEMPERATURE, THE UNITS TO BE ADDED TO THE FIFTH DECIMAL PLACE

n	C	D	F
1.60	0.25	0.29	0.40
1.50	0.26	0.30	0.42
1.40	0.28	0.33	0.45
1.30	0.30	0.35	0.49

The value in second, third, and fourth columns are the correctness to be applied per degree for the spectrum lines C, D, F

respectively. The first column n is the value obtained from the value of i in actual experiment given for 20° .

Suppose an experiment at 25° using D light gave a value of n 1.53107, then the correction would be $(25 - 20) \times 0.30 = 1.5$. This has to be added to the *fifth* decimal place of the original value of n , hence n_D (at 25°) = 1.531085.

Exercise—Given the following atomic refractivities for D line: C = 2.501, H = 1.051, O (in OH) = 1.521.

Compare the molecular refractivity calculated from the above with that obtained in actual experiment.

When hydrogen lines are used, the reflecting prism is not required. The Geissler tube is clamped in position and the beam of light focussed by means of lens P on to the slit in the wooden cap over the cell. The visible lines may be made sharp by means of a diaphragm fitted on to the lens. On looking through the telescope the chief lines visible are on the extreme right, the red line C, a pale blue line F; and on the extreme left two violet lines, G', and G''; other lines (green) are usually also visible, due to mercury vapour. Only C and F lines are used experimentally. The values of i are determined for C and F separately by arranging the intersection of the cross wires on the upper edge of the respective lines.

Having fixed the graduated disc for, say, line C, the measurement for F can be made by means of the fine adjustment G.

Experiment to Determine the Refractive Index of Acetone for C and F Lines—On examining the tables it will be observed that corrections have to be made for C and F lines, in units of the fifth decimal place. Example, where the correction is given, 0.589, the correction to be made is 0.00589.

In the case C line the correction must be *subtracted* from the value of n_D .

In the case of F (or G') line the correction value must be *added* to the value of n_D (the values of n for D, C, and F lines respectively are usually indicated thus: n_D , n_C , n_F).

Note—Whether the correction is added or subtracted from the value for n_D depends on the relative positions of C and F lines with respect to D in the spectrum.

Refractivity of Substances in Solution—The refractivity of a soluble substance can be determined from the refractivity of its solution and solvent, provided the solution is not too strong.

Let n_1, n_2, n_3 be the refractive indices of the solute, solvent, and solution respectively; and d_1, d_2, d_3 the corresponding densities, and x the percentage of solute in solution.

Then using Lorentz and Lorenz formula—

$$\frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{1}{d_1} = \frac{100}{x} \frac{n_3^2 - 1}{n_3^2 + 2} \cdot \frac{1}{d_3} - \frac{n_2^2 - 1}{n_2^2 + 2} \cdot \frac{1}{d_2} \cdot \frac{100 - x}{x};$$

or Gladstone and Dale's formula, we get—

$$\frac{n_1 - 1}{d_1} = \frac{n_3 - 1}{d_3} \cdot \frac{100}{x} - \frac{n_2 - 1}{d_2} \cdot \frac{100 - x}{x}.$$

Experiment to Determine the Molecular Refractivity of Sodium Chloride—Make up a 10 per cent. solution, and first determine its density at 25° relative to water at 25°.

Then determine the refractive index of pure water and solution respectively for the D line at 25°. Calculate the specific and molecular refractivities of sodium chloride, using Gladstone and Dale formula.

CHAPTER IX

ROTATION OF THE PLANE OF POLARIZATION

THE refractivity of liquids and dissolved substances is general; but when we come to the *polarization* of light, we are dealing with a property possessed only by comparatively few liquids and dissolved substances. This property depends entirely on the arrangement of the atoms in the molecule—for example, isomeric substances have usually very similar refractive properties, but it often happens that they behave very differently with respect to polarized light.

Polarized light (light in which the vibrations lie all in one plane) is obtained by passing monochromatic light through a Nicol prism (or tourmaline plate), which cuts off all rays except those vibrating in one plane. This prism is termed the *polarizer*. The light then passes on, and is examined by a second Nicol prism, termed the *analyzer*.

When these two prisms have their axes at right angles, the field of view is totally dark. If when such conditions exist a tube containing cane sugar solution be interposed, the field becomes illuminated, but it becomes dark again on rotating the polarizer through a certain angle. What has happened is, the plane polarization has been twisted through a certain angle by the cane sugar solution. The analyzer has therefore to be turned through a certain angle, in order to take up the previous position relative to the plane of polarized light.

The actual angle depends on the nature of the liquid, on the wave length of the light used in the measurements and on the temperature, and is proportional to the length of the tube containing the liquid under examination.

Specific rotation is defined as the angle of rotation produced by a liquid, which in a volume of 1 c.c. contains 1 gram of active sub-

stance, when the length of the column is 1 *dec.*, and is represented thus—

$$[\alpha]_D^t = \frac{100\alpha}{ld},$$

where α is the observed angle, l is the length of the column in decimetres, d is the density of the liquid at temperature t ; D indicates that sodium light was used as a source of illumination. For solutions the specific rotation is—

$$[\alpha]_D^t = \frac{100\alpha}{xld},$$

where x is the number of grams of solute in 100 grams of solution.

Polarimeter—The types now largely in use are those designed by Lippich and Laurent. The two forms only differ in the mode of production of the half-shadow. The sodium light enters through a diaphragm, which is provided with a plate (or solution) of a crystal of potassium bichromate, which filters out any extraneous light which accompanies the yellow light.

On leaving the lens E the rays pass parallel into the Nicol prism D , and then enters the second diaphragm, F , half of

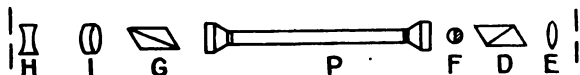


FIG. 33

which is covered with a quartz or mica plate of definite thickness, and cut parallel to the axis. From here the rays pass through the liquid tube P into the analyzer G , and then through the lenses I and H of the telescope through which the observations are made (see Fig. 33).

The characteristic part of the apparatus is the quartz or mica plate, the thickness of which is chosen so that the rays of sodium light which passes through suffers a change of phase of *half a wave length*, but still remains plane polarized. Thus we have two beams of polarized light, one double the wave length of the other. If the *polarizer* is adjusted so that the plane of polarization of light is *parallel* to the axis of the

quartz, then for each position of the *analyzer* the two halves of the field of view will be equally illuminated. If, however, the polarizer is placed at *an angle* with this axis, the plane of polarization of the rays of light which pass through the quartz plate will suffer a like displacement, but in the opposite direction.

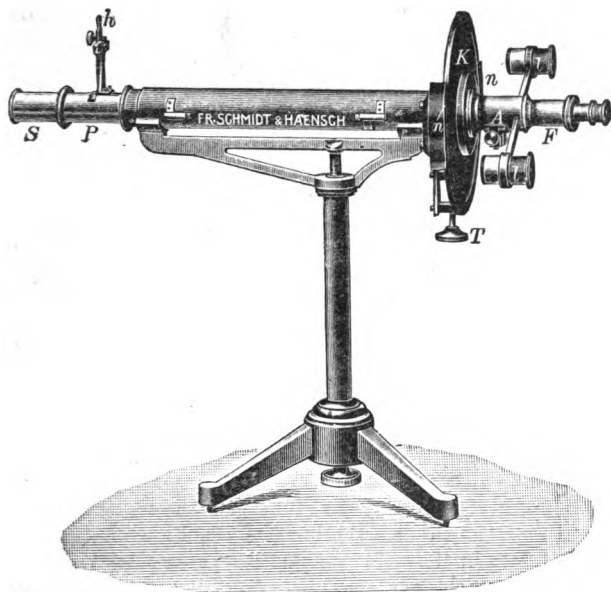


FIG. 34

When such conditions exist, the circular field appears divided into two halves, which are, with two exceptions, unequally illuminated. For two positions, however, 180° apart, both halves are equally illuminated. The apparatus (see Fig. 34) is so constructed that the analyzer, fastened to the telescope and vernier n , can be moved by means of an arm, T , on a fixed circle, K ; the vernier can be read by means of a telescope.

As already mentioned, the plane of the polarizer must form an angle with the axis of the quartz plate, thereby producing unequal illuminations of the two halves of the field. This is

accomplished by means of a contrivance, h , by means of which the polarizer can be rotated. The apparatus is first adjusted to the parallel position, so that for any position of the analyzer the two halves of the field view are equally illuminated. The polarizer is then rotated through an angle, θ , by means of h (see note). The smaller the angle is, the more sensitive is the instrument; the more brilliant the light and the clearer the liquid, the smaller θ can be made. The proper adjustment of the polarizer is that position corresponding to the greatest change of the shade in the field of view for a slight movement of the analyzer.

At the beginning of an experiment the telescope F is focussed sharply on the diaphragm, so that the dividing line at the edge of the quartz plate appears quite sharp.

In determining the *zero-point* the tube should be filled with distilled water, in order that the intensity of the light may be the same as when the active liquid is observed. In case the field of view is too dark, on account of the liquid being coloured or not clear, the illumination may be increased by a slight rotation of the polarizer; this, however, as before mentioned, renders the instrument less sensitive.

The angle θ through which the polarizer is rotated is called the half-shadow angle.

Since the quartz disc is fixed, only one wave length of light can be used with any one instrument, and the quartz disc being definitely gauged to just half this wave length.

The apparatus described above is the Laurent type. The Lippich differs in that the quartz plate is replaced by a third Nicol prism, which covers half the field of view. This apparatus has the advantage over the Laurent type, in that homogeneous light of any wave length can be used.

The observation tubes in which the liquid is placed usually consists of a thick-walled glass tube, with accurately ground ends closed by circular glass plates. These plates are held in position by means of screw caps. The tubes are either 1 dm. in length, or some simple multiple of a decimetre.

In constant temperature experiments the tube is surrounded with an outer jacket, through which water from a thermostat can be circulated (see Figs. 35, 36).

Experiment to Determine the Specific Rotation of Cane Sugar—Dissolve 10 grams of cane sugar in a little water and make up to 100 c.c. Then, having determined the zero with distilled

water in the observation tube, fill up the tube completely (free from air bubbles) with cane sugar solution (first wash the tube out with the solution). Then determine the angle of rotation—i.e., redetermine the position of equal illumination. Then from this angle calculate the specific rotation. For accurate experiments a jacket tube should be used, through which water is circulated from a thermostat. For ordinary purposes the temperature of the room is sufficiently constant.

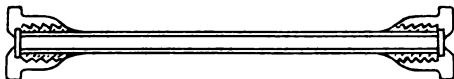


FIG. 35

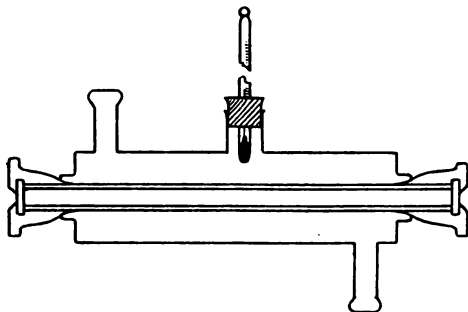


FIG. 36

To Determine the Amount of Pure Cane Sugar in a Sample of Sugar—The sugar will contain mainly cane sugar and a small amount of invert sugar, also traces of optically inactive substances which do not materially affect the experiment.

Weigh out the two samples of sugar, each 10 grams weight. One sample dissolve in distilled water, and make up to 100 c.c. The other dissolve in about 50 c.c. of water, add 10 c.c. of strong hydrochloric acid, and heat up to about 70° for ten to fifteen minutes, and then make up to 100 c.c. Now determine the angle of rotation of each sample separately. In the first case the value will be for impure cane sugar, and in the second case for invert sugar only.

For cane sugar—

$$[\alpha]_D^t = 66.5 - 0.0184(t - 20).$$

For invert sugar—

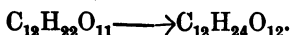
$$[\alpha]_D^t = -19.66 - 0.0361 C' - 0.304(t - 20).$$

The influence of concentration is greater in the second case, and has therefore to be taken into consideration (C').

Suppose C grams of cane sugar in the sample. Then C' grams of invert sugar result; then—

$$C' = \frac{360}{342} C,$$

since—



If α' is the angle after inversion—

$$\alpha' = - \{19.66 + 0.0361 C' - 0.304(t - 20)\} \frac{Cl}{100} + \beta.$$

$$\alpha = \{66.5 - 0.0184(t - 20)\} \frac{Cl}{100} + \beta,$$

where α is the angle of the original solution, and β the angle due to the presence of impurity (invert sugar) in the initial sugar, t is the temperature of experiment, then—

$$\alpha - \alpha' = \left[\frac{Cl}{100} \{66.5 - 0.0184(t - 20)\} \right] + \left[\{19.66 + 0.0361 C' - 0.304(t - 20)\} \frac{Cl}{100} \right].$$

Substituting $C' = \frac{360}{342} C$, we get—

$$\alpha - \alpha' = \frac{Cl}{100} [\{66.5 - 0.0184(t - 20)\} + \{19.66 + 0.0380 C - 0.304(t - 20)\} 1.0526],$$

from which C can be calculated, and hence C' .

Note—The action of the quartz plate may be explained as follows:

The plane of polarized light falling on the plate is decomposed into two rays. The two rays traverse the plate with

different velocities, and the thickness of the plate is so arranged that a difference in phase of half a wave length is produced. The effect of this is, that if the light passing through the uncovered portion of the field polarized in direction OB , making an angle θ with OA (the edge of the quartz plate), then that which has passed through the plate is polarized in a direction

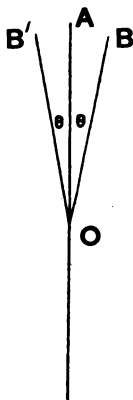


FIG. 37

OB' , so that $BOA = AOB'$. On looking through the eyepiece the two halves of the field will be unequally illuminated, unless the principal plane of the analyzing Nicol in the eyepiece make equal angles with OB and OB' —i.e., is parallel to or perpendicular to OA . In the former case the field will be equally bright, in the latter equally dark (see Fig. 37).

CHAPTER X

SPECTRUM ANALYSIS

THE *spectroscope*, next to the balance, is the most important instrument of the chemist. By its aid a chemist is able to identify substances which heretofore were entirely beyond his ken. It has long been known that certain chemical substances, when strongly heated in the almost colourless flame of a bunsen or blowpipe, impart a characteristic colour to the flame. For example, sodium salts colour the flame intense yellow, while potassium salts impart a violet colour to the flame. If, however, sodium and potassium are present in the same substance, then the intensity of the sodium yellow completely masks the violet of the potassium. Hence by this method it is impossible to detect potassium in presence of sodium with the naked eye. This difficulty is overcome by regarding the flame through a prism instead of with the naked eye. By this means the light is refracted, each differently coloured ray having its own specific refractivity. If the source of light be white, then a continuous band of differently coloured rays is observed, the white light being resolved into its various coloured constituents. The coloured band thus obtained is called a *spectrum*, and white light gives a *continuous spectrum*, stretching from red (which is the least refrangible) to violet (the most refrangible). If, now, the light from a coloured flame be allowed to fall through a narrow slit on to the prism, we get a spectrum which consists only of a few bright-coloured bands. Thus the yellow sodium flame, when treated in this way, gives two bright yellow lines close together, while the violet flame of potassium gives two bright lines, one in extreme red and the other in extreme violet. These peculiar lines, or sets of lines, are absolutely characteristic of the chemical element in question, and are

exhibited by no other substance ; further, the position of each line in the spectrum is definitely fixed, and never alters for any given apparatus. Hence, suppose we examine the flame given by a mixture of sodium and potassium salt, we see the red and purple lines in their respective portions of the spectrum, and the yellow sodium lines in between, just as distinctly as when only one element is there alone. Some elements give a great many coloured bands, but no matter, the same element will always give exactly the same number of bands, in precisely the same position, no matter what the source of the element originally may be. If a number of elements are present, then the spectrum is made up of the spectrum of each separate element, and in most cases the spectrum can be analyzed into groups, and the elements in this way identified ; in other words, an analysis of the mixture can be made.

A great advantage of this method of analysis is its extreme delicacy, as well as in the great facility with which the presence of particular elements can be detected with certainty. Thus the $\frac{1}{180,000,000}$ of a sodium salt can be detected ; lithium to the extent of 1 part in 6,000,000. In this way the presence of substances can be made manifest where hitherto they have eluded detection. For example, lithium, which was formerly supposed to exist only in four minerals, has been detected in almost all spring waters, in tea, tobacco, milk, and blood.

Again, certain samples of sodium and potassium exhibited certain lines which were entirely absent in other samples, yet the additional lines did not belong to any then known substance. What was the result of this observation ? The discovery of the alkali metals, rubidium and cæsium, in 1860 by Bunsen. These metals had previously eluded detection simply because they occurred in such minute quantities that it was absolutely impossible to detect them by ordinary analytical methods. Since Bunsen's discovery of rubidium and cæsium the spectroscope has been the means of revealing quite a number of previously unknown elements.

It is not only those bodies which have the power to impart colour to a flame which yield characteristic spectra, this property belongs to every elementary substance, whether metal, non-metal, solid, liquid, or gas ; and it is always observed when such an element is heated to the point at which its vapour becomes luminous, for at this point each

element emits its own specific light, and the characteristic bright lines are apparent on observing the spectrum.

The majority of the metals require a much higher temperature than the ordinary flame in order to make their vapours luminous; they may, however, be easily heated up to the required temperature by means of an electric spark, which volatilizes a little of the metal in passing between two points, and heats it to an intensity sufficient to enable it to emit its own peculiar light. Thus, all metals (including iron, platinum, gold, silver, etc.) can be recognized by means of their spectra.

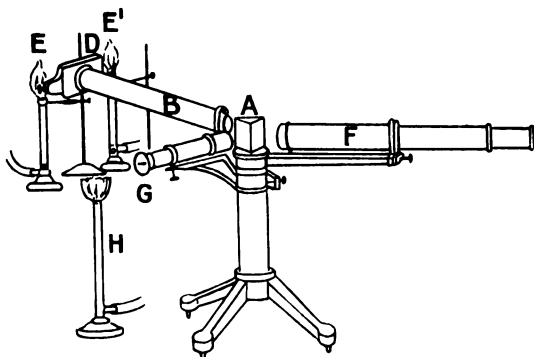


FIG. 38

The permanent gases, such as hydrogen, can be rendered luminous by means of an electric spark, and their spectra mapped out. Thus the red light of the incandescent hydrogen is resolved into one bright red, one blue, and two violet lines. There are two distinct types of spectra—namely, *line spectrum*, which is made up of a number of sharply defined coloured lines (really images of the slit), and *band spectrum*, which consists of bands which are broad, even with a very narrow slit. These bands are often sharp on one side, and gradually fade away on the other.

The Spectroscope—This instrument is somewhat as shown in Fig. 38. It consists of a prism, *A*, which is firmly fixed on an iron base; a collimator, *B*, which carries an adjustable slit at one end and a lens at the other end, by means of which the

light from the coloured flame *E* is rendered *parallel* before falling on the prism *A*. The light, having been refracted by the prism, is received by the telescope *F*, and the image magnified before reaching the eye. In many instruments the slit is half covered with a small prism. By this means it is possible to obtain two spectrum bands at the same time from two different flames. One is arranged so that the rays pass directly through the uncovered portion of the slit. The rays from the second flame first strike the small prism, and are then *reflected* through the slit and along the collimator on to the prism. Usually one flame gives a standard spectrum, which helps to emphasize any special characteristics of the substance tested. The tube *G* contains a scale which is illuminated by the white light from *H*. This scale is distinctly visible in the telescope, and by it the position of any coloured spectrum line can be definitely fixed.

Adjustment of the Spectroscope.—It has already been pointed out that the rays of light leaving the collimator should be

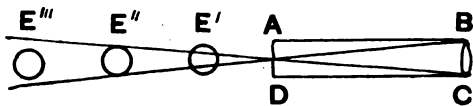


FIG. 39

parallel. This is achieved by adjusting the distance between the slit and the collimator lens. First bring the spectroscope near a window, and observe through the telescope some distant object; focus the telescope by means of the adjusting screw until that object is seen clearly. The telescope is then focussed for parallel light. Now bring the telescope into the dark-room, and illuminate the slit of the collimator by means of a sodium flame; then adjust the collimator by sliding it in or out until the image of the slit is seen quite sharply. Now illuminate the scale, and adjust it so that the sodium line is about a third the distance from the left-hand side of the scale. Remember it is necessary to have the spectra as bright as possible. This depends upon the position of the sodium flame relative to the slit. The importance in securing the correct position of the flame will be better understood from Fig. 39. Let *A*, *B*, *C*, *D* represent a section of the collimator, *B*, *D* the lens, and *S* the slit, also *E'*, *E''*, *E'''*—three different positions

of the flame. At position E' only part of the flame is used to illuminate the collimator; at position E'' the outside portions of the lens are not illuminated at all. It is only at the position E'' that the lens is illuminated with the maximum amount of light. This position must in all cases be determined by trial.

Mapping of Spectra.—Prepare several pieces of platinum wire (thickness 1 mm.) sealed into glass tubes. Clean them thoroughly by moistening with pure concentrated hydrochloric acid and heating white heat in bunsen. Repeat this process until the wire imparts no coloration to the bunsen flame. The student should also provide himself with a sheet of paper on which are ruled lines divided into millimetre divisions. Now take one of the wires and moisten it with pure concentrated hydrochloric acid, dip the wire into a little solid sodium chloride, causing a little to adhere to the wire. Now place the wire in the hottest part of the flame—i.e., just above the cone (this portion of the flame should be adjusted so as to be opposite to the slit)—and observe the position of the sodium line on the scale. Mark the position on one of the lines on your scale-paper, each division on your scale corresponding, say, to 1 mm. on your paper. On a second wire, moistened with hydrochloric acid, place a small quantity of barium chloride, and in a similar manner map out the spectrum. One, and perhaps two, bright green lines should be visible in this case; if this is not so, the slit requires adjusting. Repeat this with fresh platinum wires with the chlorides of lithium, thallium, strontium, calcium, and potassium. In the case of potassium there is a very distinct red line and also a line in the violet, but this is often very difficult to see, except by experienced observers. The violet can usually be seen by removing the light which illuminates the scale and readjustment of the slit; then, having noted its approximate position, it can often be detected on illuminating the scale again, and hence its position obtained.

In the case of calcium and other salts it will be observed that the spectrum changes. The first spectrum is due to the chloride, which is gradually replaced by that of the oxide.

The spectrum of an incandescent *solid* is continuous; a discontinuous spectrum of bright lines is only produced by an incandescent *gas*. The yellow line seen when a salt of sodium is heated on a platinum wire in the bunsen flame is due to the

vapour of sodium set free by the temperature of the flame, or by chemical change taking place between the substance and the hot gases of the flame. The carbonates, chlorides, or nitrates of the alkaline earths are convenient to use, but the chlorates, where possible, are preferable, since as a consequence of the liberation of oxygen the flame is hotter.

The actual number of lines visible depends upon the temperature of the flame. Thus a flame of hydrogen burning in chlorine does not give the sodium line when sodium is intro-

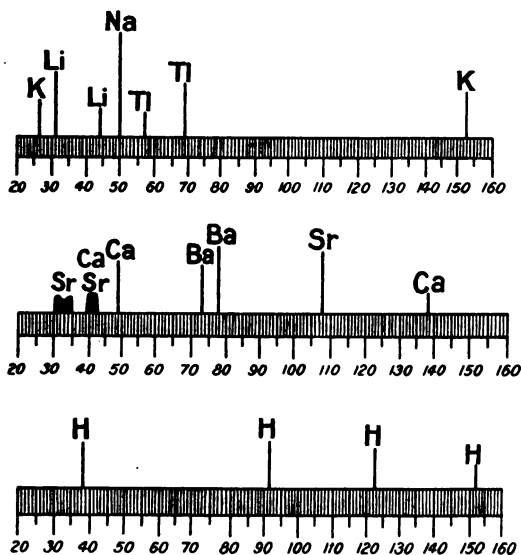


FIG. 40

duced into it; or, again, the sodium line is hardly visible in a flame of sulphuretted hydrogen burning in air. If, on the other hand, much hotter flames are used, such as the oxy-hydrogen flame, then new lines are revealed. Thus, with such a flame sodium gives five lines at 43.2, 50.0, 56.0, 76.0, 83.6, whereas in the electric spark spectra of sodium eight lines are visible.

Bunsen flame spectra are somewhat as follows (Fig. 40):

Sodium—A bright yellow line at position 50·0. This line is a standard, and is known as the D line.

Lithium salts colour the flame crimson. The spectrum consists of two lines, a very brilliant one at 31·7, and a much feebler line at 45·0. The red line should be quite distinct.

Potassium gives one line in the extreme red at 17·5, and another in the extreme violet at 153·0.

Alkaline Earths—The spectra of the alkaline earths are not so simple as those of the alkalis. When first introduced into the flame there are seen certain bands which are different according to the particular salt of the metal used, and which are supposed to be due to the compound employed, but the final spectrum is the same with all salts, which is partly due to the oxide, besides which the brightest lines of the metal are also visible.

Calcium is recognized by its characteristic orange band, 40·0-43·0, and the green band, 61·0-63·0. Chloride, chlorate, bromide, give the best results. Non-volatile salts should be treated with hydrochloric acid if it decomposes them, or heated with ammonium fluoride.

Strontium gives an orange band at 44·0-47·0, red lines 30·0-35·0, but the most characteristic is the blue line at 107·6. The best salts to use are chloride or chlorate; the lines are not visible with silica, silicate, phosphate, etc.

Barium gives brilliant green bands at 73·0 and 78·0.

Hydrogen Spectrum—In the case of hydrogen, the spectrum is obtained by using exhausted tubes, such as Geissler or Plucker tubes. Such a tube is shown in Fig. 41. The electrodes of platinum are sealed into the glass, one at each end of the tube, and the central portion is a capillary tube. It is the capillary portion which is placed in front of the slit of the spectroscope, while a discharge is passed through the tube by means of an induction coil. If the tube contains "rarefied" hydrogen, then the discharge is red, which, when observed through the spectroscope, shows the red (*C* line) at 34·0, blue (*F* line) at 92·0, and two violet (*G* *G'* lines) at 127·5 and 151·0 respectively. The red and blue are the most conspicuous.



FIG. 41

The student should obtain such a tube and map out the spectrum as before.

Reduction of Spectroscopic Measurements to an Absolute Scale—When the spectrum of a given substance is mapped, the relative positions of the lines will be found to differ according to the instrument used. Even if the sodium line is at the same scale division in each, the readings of the other lines will differ in the different instruments, since they depend upon the dispersion of the prism and on the distance between the divisions of the scale. The student must not, therefore, expect his readings to coincide with the scale number here given as examples, as this, except by mere coincidence, will not be the case. The numbers and positions of the lines on the diagrams are for one particular prism and for one particular scale. The student will therefore at once see the importance of being able to standardize his readings so that they may be comparable with the readings obtained on *any* other instrument. In other words, the student must be able to represent his results in a manner which is entirely independent of his instrument. This is done by reducing the measurements taken on the arbitrary scale to wave lengths. There are several methods by which this may be done, but only one need be considered here—namely, what is known as the *graphical interpolation method*. In this method the positions of three (or more) lines, the wave lengths of which are known, are observed on the arbitrary scale of the spectroscope, and the unknown wave lengths of other lines are obtained by interpolation.

For our purpose we will take six standard lines of known wave length, whose position on the scale of a certain instrument are as quoted—viz. :

The Chloride of—			Line taken	Wave Length	Scale Reading
Potassium	...	...	Red	7669	17.5
Lithium	...	...	Red	6708	31.7
Strontium	...	...	Orange	6409	40.0
Sodium	...	...	Yellow	5893	50.0
Thallium	...	...	Green	5351	69.0
Strontium	...	...	Violet	4608	107.6

The wave lengths are given in Angström units, where 1 unit = $\frac{1}{10\,000.000}$ mm. ($0.1\ \mu\mu$). Having noted the position of the

above six lines on the scale, and given their wave lengths, it is only necessary now to draw a curve, the scale readings taken as the abscissæ, and the corresponding wave lengths as ordinates (see Fig. 42); connect the separate points by a smooth curve, 1 mm. representing one division on the scale, and, say, 1 mm. on the ordinate representing 40 wave-length units. From this curve the wave length may be read that corresponds to each division on the scale.

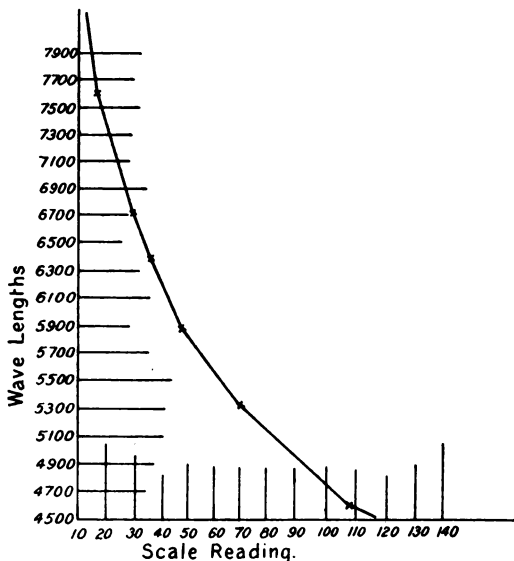


FIG. 42

Exercise: Determine the Wave Lengths of—

- (a) Hydrogen (*C* and *F* lines).
- (b) Barium (green lines).
- (c) Calcium (orange lines).

The student should now try one or two "unknowns," selected from those whose spectrum he has already mapped, by first mapping the spectrum of the unknown, and then, by comparison with the spectra previously prepared, determine what the metal is.

If time permits, he should map the spectrum of a mixture of two or three metals.

CHAPTER XI

DETERMINATION OF PARTITION COEFFICIENTS

Distribution of a Substance between Two Non-Miscible Solvents—When succinic acid is shaken up with two immiscible liquids, such as ether and water, the distribution which takes place is very similar to the distribution of a substance between a liquid and a gas phase (solution of a gas in a liquid), and therefore similar rules apply to the distribution of a substance between two immiscible solvents as to the solution of gases. These may be expressed as follows :

1. If the molecular weight of the solute is the same in both solvents, the distribution coefficient (*i.e.*, the ratio in which the *solute* distributes itself between the two *solvents*) is constant at constant temperature (Henry's law).

2. In the presence of several solutes the distribution of *each* solute separately takes place as if the others were entirely absent. (This corresponds to Dalton's law of partial pressure.)

3. The ratio in which the solute is distributed between two solvents depends, however, not only on its solubility in each solvent, but also on whether it possesses the same molar weight in the two solvents. Hence a study of these relationships is of vital importance, in so far as they afford a means of determining the state of association or dissociation of a substance in solution.

This will be better understood from a consideration of the following results given by Nernst :

Distribution of Succinic Acid between Ether and Water—Varying quantities of succinic acid were shaken up with water and ether and the distribution coefficient determined where C_1 is the concentration in water and C_2 the concentra-

72 DETERMINATION OF PARTITION COEFFICIENTS

tion in ether. The approximate constancy of this ratio shows that Henry's law applies.

C_1 (Water)	C_2 (Ether)	$\frac{C_1}{C_2}$
0.024	0.0046	5.2
0.070	0.013	5.2
0.121	0.022	5.4

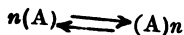
When, however, *benzoic acid* is shaken up with *benzene* and *water*, Nernst gives the following results :

C_1 (Water)	C_2 (Benzene)	$\frac{C_1}{C_2}$	$\frac{C_1}{\sqrt{C_2}}$
0.0150	0.242	0.062	0.0305
0.0195	0.412	0.048	0.0304
0.0289	0.970	0.030	0.0293

It will be observed that in this the ratio $\frac{C_1}{C_2}$ is not constant, but the ratio $\frac{C_1}{\sqrt{C_2}}$ is constant.

These results show that while benzoic acid has a normal molecular weight in water, it consists almost entirely of double molecules in benzene. In such a case the concentration of the *single* molecules in benzene is proportional to square root of the total concentration. Since a constant ratio should be found between the concentration of the single molecules in the first solvent and the single molecules of the second solvent, it follows that $\frac{C_1}{\sqrt{C_2}}$ must be a constant (Law of Mass Action, Dilution Law, etc.).

Generally this law may be stated, that if in one solvent the solute is present as simple molecules, and in the second solvent in "*n*" simple molecules are associated as



and C_1 is the concentration in the first solvent and C_2 in the second, then the ratio $\frac{C_1}{\sqrt[n]{C_2}}$ should be a constant.

Experiment to Determine the Distribution Coefficient of Succinic Acid between Ether and Water—Take a well-stoppered bottle, and introduce 100 c.c. of distilled water (free from CO_2) in which 1 gram of succinic acid has been dissolved. Add an equal volume of ether. Fix the stopper securely, and immerse the bottle up to the neck in a thermostat at 25°C . Shake the bottle vigorously every five minutes for about forty minutes. Determine the concentration of acid in each layer by carefully removing 25 c.c. of solution with a pipette. The titration should be done with $\frac{n}{20}$ baryta solution, using phenolphthalein as an indicator.

Repeat the experiment, using 2 per cent. and 5 per cent. solutions respectively, and determine in each case the value of the ratio $\frac{C_1}{C_2}$.

Experiment to Determine the Distribution Coefficient of Benzoic Acid between Water and Benzene—Prepare three solutions of benzoic acid in benzene containing 12, 6, and 3 per cent. of benzoic acid respectively. To 100 c.c. of benzene solution add 100 c.c. of distilled water, and proceed exactly as in the previous experiment. Since at the concentrations used in these experiments benzoic acid exists mainly as $(\text{C}_6\text{H}_5\text{COOH})_2$ —i.e., associated molecules in the benzene solution—the ratio $\frac{C_1}{\sqrt[n]{C_2}}$ should be constant.

Experiment to Find the Degree of Association of Benzoic Acid in Chloroform—Repeat exactly the previous experiment, using chloroform instead of benzene, and find what value of n in the ratio $\frac{C_1}{\sqrt[n]{C_2}}$ gives a constant. This value is the number of molecules which are associated in the chloroform solution.

CHAPTER XII

THERMO-CHEMICAL MEASUREMENTS

Hess's Law—When the same chemical change takes place between two definite amounts of two substances *under the same conditions*, the same amount of heat is always given out, provided that the final products or product are the same in each case.

The actual heat effect, absorbed or evolved, depends on (a) the nature of the reaction, (b) the physical conditions of the reacting substances, and (c) the amounts of the substances present. Usually the heat of a reaction is measured by the method of mixtures.

The value of the thermal effect measured in calories (cal.) is usually too large, and the last figure uncertain, so a larger unit is used, equal to 100 cals. This larger caloric is usually represented by K, and is practically equal to the amount of heat required to raise 1 gram of water from 0° to 100°. A larger caloric still, due to Berthelot, is now considerably used, and is equal to 1000 calories, and is represented by *Cal.*, as distinguished from *cal.*

Heat of Neutralization—By the heat of neutralization of a monobasic acid and a base is meant the amount of heat given out when 1 gram molecule of acid and 1 gram molecule of the base, dissolved in water, are mixed.

For polybasic acids, as many heats of neutralization are possible, as there are basicities for each acid.

The reaction is caused to take place in a calorimeter, which should be preferably of platinum or silver, but nickel, copper, or aluminium may be used. It should have a capacity of about 600 c.c. The outer surface of this calorimeter should be polished. This is then surrounded by at least two other vessels, polished on the inside, and, if possible, a water-jacketed

vessel should surround these. In each case the respective calorimeters are insulated from one another by wooden blocks. The two inner vessels should be fitted with non-conducting lids, with two holes in each, to admit a stirrer (glass) and a thermometer, reading at least in tenths (better use a Beckmann).

Experiment to Determine the Heat Neutralization of Hydrochloric Acid by Caustic Soda—Prepare 250 c.c. of a semi-normal solution of caustic soda and hydrochloric acid, and determine accurately the strength. The caustic soda should

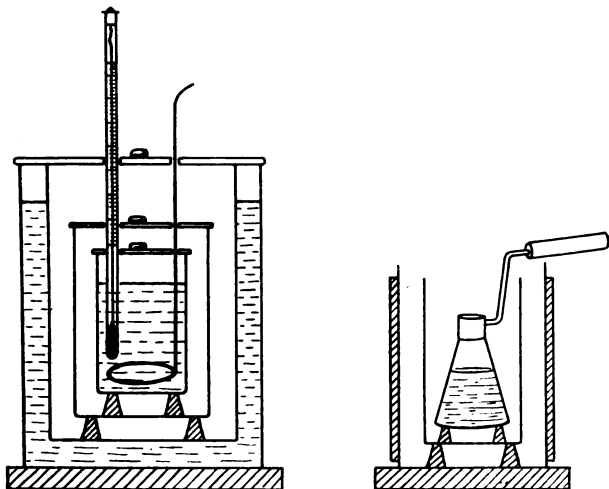


FIG. 43

be free from carbonate. Fit up the apparatus as shown in Fig. 43, and measure out into the inner calorimeter 250 c.c. of caustic soda.

Into a flask (previously washed out with $\frac{n}{2}$ HCl), protected with at least two polished metal cylinders, to reduce loss by radiation, introduce 250 c.c. of hydrochloric acid. A sensitive thermometer (graduated at least in tenths) is supported in the hydrochloric acid. This thermometer must have been previously compared with that in the alkali. In order to allow for the loss of heat by radiation, it is necessary to determine the rate of change of temperature of both a

and alkali before mixing, and then of the mixture by taking readings, say every minute, for about seven minutes before the solutions are mixed, then mix the solutions quickly, constantly stirring, and again take readings for a similar period. (Note— t_1 should be as near as possible equal to t_2 .)

In order to determine the true temperature which should have resulted, it is necessary to plot the above readings. This is illustrated in Fig. 44.

The curves t_1 and t_2 give the temperatures for alkali and acid respectively. After seven minutes, the solutions are

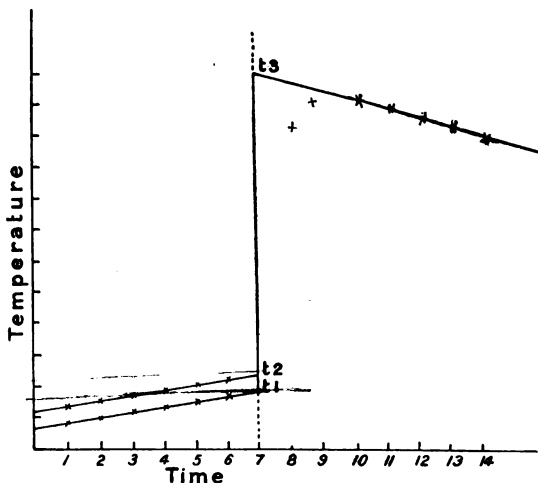


Fig. 44

mixed, then the temperature continues to rise, rapidly at first, for about three minutes, after which it falls gradually.

The bend in the curve is obviously due to loss by radiation whilst the mixture was becoming heated, since a time-cooling curve would be straight. The direction of the true curve is, however, given by the last few readings. Hence, by extrapolation, the true elevation temperature, t_3 , can be found by drawing a perpendicular at the point which indicates the instant of mixing (seventh minute), and reading off the temperature at the point where this line cuts the extrapolated

cooling curve—i.e., the temperature reading thus obtained is used in calculating the result.

Calculation—The heat evolved is represented by the following equation—

$$q = (m_1\alpha + m_2\beta + m_3\gamma + m_4\delta) \left[t_3 - \left(\frac{t_2 + t_1}{2} \right) \right],$$

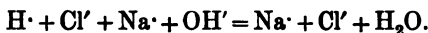
where m_1, m_2, m_3, m_4 are the masses of the solution, calorimeter, thermometer, and stirrer respectively, and $\alpha, \beta, \gamma, \delta$, their respective specific heats.

As regards the solution, it will be sufficiently accurate in this case to take the water equivalent of the solution as equal to the mass of water contained in it—i.e., equal to the volume of the solution approximately. In the case of the thermometer we do not know the relative weights of the glass and mercury, but we may make use of the fact that, volume for volume, the specific heats of glass and mercury are practically identical, and equal to 0.47 per c.c.

To find the volume of the thermometer immersed in the solution insert it in a burette, partially filled with water, up to the depth it is immersed in the solution, and measure the displacement. If the thermometer is not solid, as in the case of a Beckmann, the volume of the bulb and the requisite portion of the stem must be found separately, and the volume found for the stem divided by five, and this value added to the volume for the bulb.

In place of the ordinary calorimeter a Dewar vacuum vessel may be conveniently substituted, to reduce the loss of heat. *Repeat the above experiments, using ammonium hydroxide and sulphuric acid, also caustic potash and acetic acid.*

In accordance with the theory of electrolytic dissociation, the heat of neutralization of any completely dissociated base is constant, since the reaction consists solely of the union of H^+ and OH^- ions giving unionized water. In the case of hydrochloric acid and caustic soda it may be represented thus—

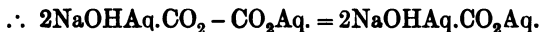


The value of this constant is 13.7.

When it is required to determine the heat of neutralization of a polybasic acid with a monovalent base, or *vice versa*, the thermal effect must be calculated for each basicity separately.

In case precipitates are formed, the heat of precipitation

must be subtracted from the heat evolved (see later section). If the acid or base is a solid or gas, a correction for heat of fusion-solution, or absorption must be applied when possible. For example, when caustic soda solution is neutralized by gaseous CO_2 , we get a certain heat effect, $2\text{NaOHAq} + \text{CO}_2$; but to get the true heat of neutralization the heat of absorption of CO_2 must be subtracted—i.e., CO_2Aq .



Heat of Solution—The heat of solution of a substance is the thermal effect produced by dissolving 1 gram molecule of a substance in a given number of molecules of solvent.

The heat of solution may be sometimes positive and sometimes negative, that is, heat may be evolved or absorbed.

It varies with the quantity of solvent used. If further dilution produces no further heat effect, the heat measured for 1 gram molecule is known as the heat of solution at *infinite dilution*.

Experiment to Determine the Heat of Solution of Sodium Chloride

—The method is similar to that employed for heat of neutralization. Into the calorimeter introduce 500 grams of water, and fit up the apparatus with thermometer and stirrer as before, taking the same precautions as to temperature readings. Weigh out into a dry test-tube 10 grams of finely powdered dry sodium chloride. Place the test-tube in a beaker filled with water at a known temperature (which should, as near as possible, be at the same temperature as the water previously weighed out). When the salt has acquired the temperature of the bath, remove the test-tube, dry it roughly, and empty the contents into the calorimeter and stir rapidly, and take readings every minute for seven or eight minutes.

Plot the temperature readings against time, and eventually determine the maximum elevation.

The method of calculation is similar to the previous experiment. Consider the solution as pure water for calculation.

Repeat the above experiment with $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Heat of Hydration—The heat of hydration is the quantity of heat liberated when 1 gram molecule of substance combines with a definite number of molecules of water to form a hydrate.

The heat of hydration is obtained by determining the heat of solution of the hydrated and anhydrous forms of the salt, and subtracting the latter from the former.

The method of experiment is therefore essentially that for determining the heat of neutralization and solution.

Experiment to Determine the Heat of Hydration of Copper Sulphate—

(a) Determine the heat of solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

(b) Determine the heat of solution of CuSO_4 .

Then $(b - a) = \text{heat of hydration}$.

Heat of Dilution—By heat of dilution is meant the quantity of heat liberated or absorbed when a solution is further diluted by the solvent.

The method here again is similar to the determination of heats of neutralization. The result is expressed as the amount of heat change resulting from a given increase of solvent. Both the initial and final concentrations must be stated in the result. It is equal to the difference between the heats of solution for the two respective volumes of solvent.

*Experiment to Determine the Heats of Dilution of a 3 per Cent. Solution of Potassium Nitrate—*Dissolve 12 grams of nitrate in 400 grams of water, and determine the heat evolved on adding 100 grams of water.

Heat of Precipitation—The heat of precipitation is the quantity of heat evolved when a gram molecule of substance separates out from a solution.

It is the converse of heat of solution, and is numerically equal to it.

*Experiment to Determine the Heat of Precipitation of Silver Chloride—*Dissolve 1 gram of sodium chloride in 500 c.c. of water, and place it in a calorimeter fitted up as before. Prepare 15 c.c. of normal silver nitrate at the same temperature. When the temperatures are equal, mix the solutions, and note the change in temperature. From the results calculate the heat of precipitation. Details of the experiment are the same as in the previous cases.

The result is the same as the heat of solution with the opposite sign.

Heat of Combustion—The heat of combustion of a substance is the quantity of heat evolved in the complete combustion of 1 gram molecule of substance.

Let x be the amount of substance used in the experiment, and M the molecular weight of the substance; also let W be the weight of water in the calorimeter, and w the water equivalent of the apparatus, T_1 and T_2 the initial and final temperature, then Q , the heat of combustion, will be given by—

$$Q = \frac{M}{x} (W + w) (T_2 - T_1).$$

The reaction is usually caused to take place in compressed oxygen inside a calorimetric bomb.

A convenient form of bomb is as shown in Fig. 45. It is known as the Mahler-Cook bomb, and is a modification of the Berthelot-Mahler bomb.

The Bomb—This consists essentially of an enamelled steel vessel, capable of withstanding high pressures.

The lower part, D , is closed by a lid, A , which is screwed on, an air-tight connection being obtained by means of a lead-washer, C . Two stout platinum wires pass through the cover, one, T , being insulated by means of a quartz plug; these wires are connected by two terminals. One of the wires is bent round in the form of a loop, so as to

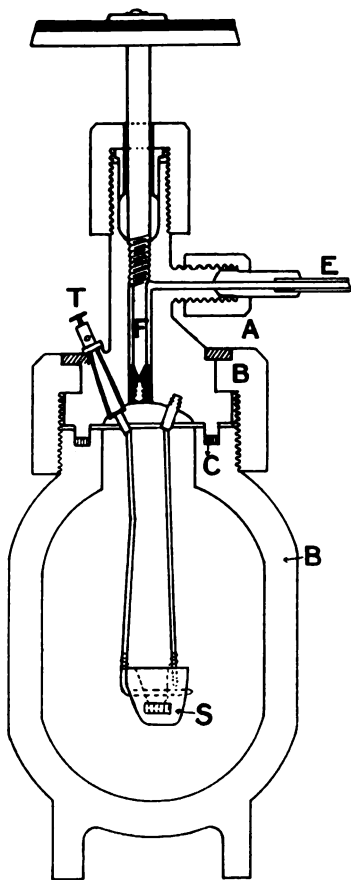


FIG. 45

support a crucible, which may be of platinum, unglazed porcelain, or silica. The substance is placed in the crucible, and the ignition is effected by means of a coil of iron wire, which joins

the two platinum wires, which is caused to burn by means of an electric current. Oxygen is admitted through a valve in the centre of the lid, the opening and closing of the valve being controlled by screw *F*. The oxygen, which is supplied from a cylinder fitted with a pressure gauge, is attached at *E*.

The Calorimeter—The calorimeter consists of a large nickel-plated vessel, *A*, to contain the water in which the bomb is to

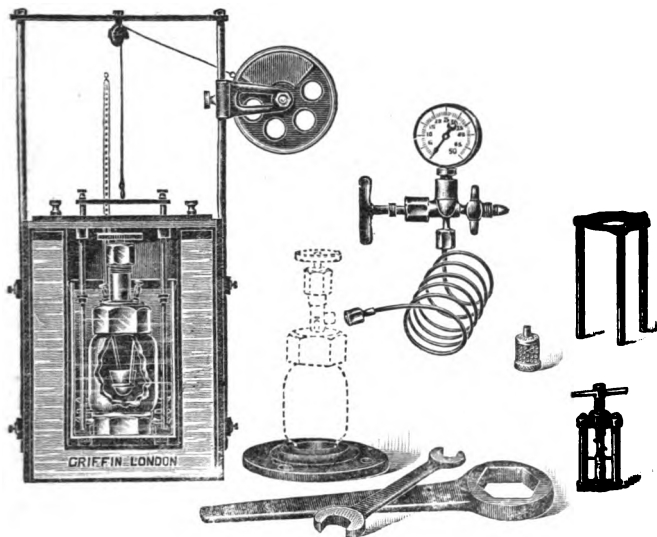


FIG. 46

be immersed. This is surrounded by an outer water-jacketed vessel. Both calorimeter and outer vessel are fitted with suitable stirring arrangements. The stirrer in the calorimeter may be conveniently worked with a small motor. On the downward stroke the stirrer should almost touch the bottom of the calorimeter, whilst on the upward stroke it should remain completely immersed in the water (see Fig. 46).

The change in temperature is read by means of a Beckmann thermometer. The outer jacket is closed with a non-conducting lid, fitted with the necessary holes for stirrer and thermometer.

The Water Equivalent of the whole apparatus is determined by means of a substance of known heat of combustion.

The heat received by the water in the calorimeter can be calculated from the elevation in temperature on combustion, and from this value and the known heat of combustion of the substance the heat taken up by the apparatus can be obtained, and hence the water equivalent.

Camphor, or naphthalene, are suitable for this purpose, and they give out 9292 and 9693 calories respectively per gram of substance.

Experiment—Open the bomb by unscrewing the nut *B* and carefully remove the cover. Place a crucible in position. Make a small tabloid of, say, camphor; weigh it accurately (use about 1 gram), and place it in the crucible. Make a short spiral of about 15 cms. of iron wire, and weigh it, and then connect it between the two stout platinum wires. The iron spiral is then pressed down until it makes a contact with the substance; the lid is then replaced, and the nut *B* screwed tightly down, the bomb being held by the bottom nut, *C*, which is fitted into a hexagonal plate fitted to the bench. The bomb is then connected at *E* with an oxygen cylinder and pressure-gauge. The valve *F* is closed, and the valve on the oxygen cylinder opened slowly; then slowly admit the gas to the bomb by opening *F*. When the pressure reaches 25 atmospheres with *F* well open, close the valve *F* tightly, and then shut off the oxygen cylinder and disconnect.

The water-jacket of the calorimeter should be filled with water several hours before the experiment is to be done.

Weigh out into the calorimeter about 2.5 kgs. of water (sufficient to immerse the bomb up to the nut *B*). The calorimeter is then placed in position, being insulated at the bottom by a wooden block or cork. To counterbalance the loss by radiation, the water in the calorimeter should be at a slightly lower temperature than that of the room—such that the temperature of the room is the mean between the initial temperature of the water in the calorimeter and the highest temperature of the experiment. The total rise is usually about 3°, therefore the initial difference should be about 1.5°. The bomb is now carefully lowered into the calorimeter and the terminals connected to the battery, the circuit being broken by a switch key. Insert the Beckmann thermometer and commence stirring. After about five minutes,

record the reading every minute for about eight minutes. At the eighth minute complete the electric circuit, thereby causing the ignition to take place. Continue to take minute readings. When the highest temperature has been reached, the readings should be continued for a further eight or ten minutes. The observations are then complete. Open valve *F* carefully, and then unscrew *B*. If any iron wire is unburnt, it must be carefully weighed and subtracted from the original weight of iron used.

The method of calculating the results will be better understood from the following example, in which the water equivalent of the apparatus is calculated by means of naphthalene :

Weight of naphthalene = 1.2966 grams.

Weight of iron = 0.1568 gram.

TEMPERATURE READINGS

I

Time in Minutes	Beckmann Reading	Δt
0	1.805	—
1	1.808	0.003
2	1.813	0.005
3	1.815	0.002
4	1.818	0.003
5	1.821	0.003
6	1.823	0.002
7	1.824	0.001
8	1.825	0.001
(circuit closed)		Mean = 0.0025

II

8	1.825	—
(circuit closed)		
9	3.814	—
10	4.536	—
11	4.998	—
12	5.514	—
13	5.666	—
14	5.700	—
15	5.706	—
16	—	—

III

Time in Minutes	Beckmann Reading	δt
16	5.706	—
17	5.706	—
18	5.705	0.001
19	5.704	0.001
20	5.703	0.001
21	5.703	0.000
22	5.702	0.001
23	5.700	0.002
24	5.697	0.003
25	5.695	0.002
26	—	—
		Mean = 0.0011

During the middle period (heating period) heat will have been lost by radiation. From Series I and III the rates of

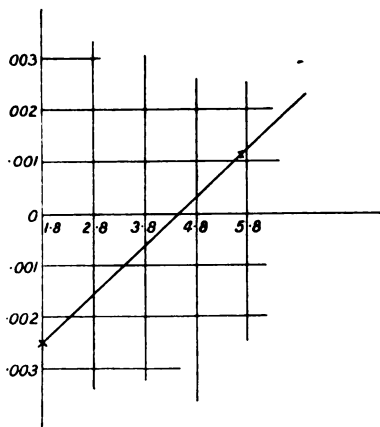


FIG. 47

cooling can be calculated. In Series I the rate of cooling is negative, denoting the temperature is rising—i.e., Δt is negative and δt positive.

Draw a cooling curve as shown in Fig. 47 by drawing a straight line through points 1·8 to 0·0025, and 5·7 to 0·0011. Then correct all temperatures in Series II from this curve.

Temperature	Cooling in Each Minute	Total Loss	Corrected Temperature
1·825	—	—	1·825
3·814	- 0·0007	- 0·0007	3·8133
4·536	0·0	- 0·0007	4·5353
4·998	+ 0·0004	- 0·0003	4·9977
5·514	+ 0·0009	+ 0·0006	5·5146
5·666	+ 0·001	+ 0·0016	5·6676
5·700	+ 0·0011	+ 0·0027	5·7027
5·706	+ 0·0011	+ 0·0037	5·7097

The values in the second column are read off from the curve.

The corrected temperature is therefore 5·7097 for the maximum. Hence the elevation = $5·7097^{\circ} - 1·8250^{\circ} = 3·8847^{\circ}$. The calorimeter contained 2500 grams of water.

The heat of combustion
of naphthalene ... = 9,693 cal. per gram.
The heat of combustion
of iron ... = 1,600 cal. ,,
Therefore heat evolved
by naphthalene ... = $1·2966 \times 9,693 = 12567·9$ cal.
Therefore heat evolved
by iron ... = $0·1568 \times 1600 = 260·9$ cal.
Total heat evolved ... = 12828·8 cal.

Of this, $2500 \times 3·8847 = 9711·9$ cal. were taken up by the water.

$$\therefore 12828·8 \text{ cal.} - 9711·9 \text{ cal.} = 3116·9 \text{ cal.}$$

Therefore 3116·9 cal. were taken up by the apparatus in rising $3·8847^{\circ}$.

$$\therefore \text{Water equivalent} = \frac{3116·9}{3·8847} = 802·3 \text{ grams.}$$

The water equivalent of apparatus = 802·3 grams.

In accurate work it is necessary to estimate the oxides of nitrogen which will have been formed during the combustion, and the heat of formation allowed for.

In the above example the water equivalent of the calorimeter was the unknown factor, the heat of combustion being known. In determining the heat of combustion the value found above will be used, leaving the heat of combustion as the only unknown.

CHAPTER XIII

DETERMINATION OF TRANSPORT NUMBERS

WHEN a current is passed through an electrolyte the numbers of positive and negative ions discharged at the respective electrodes in a given time are equal. It must not, however, be assumed that the velocities of the ions are equal, because this is not the case. The speed of the anion may be very different from that of the cation, and, in fact, this is almost invariably so. The result is, the concentration of the faster ion round the electrode towards which it travels increases. This being the case, Hittorf showed how, by experiment, the *relative speeds* of the ions could be deduced from the changes in concentration round the electrodes after electrolysis. The speed of the cation is usually represented by u , and that of the anion by v . The total amount of electricity passed through the solution is proportional to the sum of the ionic velocities—i.e., $u + v$. Of this let n be the fraction carried by the anion, then $1 - n$ will be the fraction carried by the cation, and from this it follows that—

$$n = \frac{v}{u + v} \text{ and } 1 - n = \frac{u}{u + v}.$$

The value of n is termed the *transport number* of the *anion*, and $1 - n$ the transport number of the *cation*.

The transport number can therefore be found by determining the total amount of electricity which passes through the solution and the amount of one of the ions which have passed from the solution in the immediate neighbourhood of one of the electrodes—i.e., determine the change of concentration of one of the ions round one of the electrodes. Hence, in order to investigate the changes of concentration, it is only

necessary to analyze a portion of the solution round one of the electrodes.

The above will only be correct if the liquid which is not in the immediate neighbourhood of the electrodes does not alter. This can be approximated too, if the time during which the current passes is not too long. The time should also be as short as possible so as to minimize the effect due to diffusion.

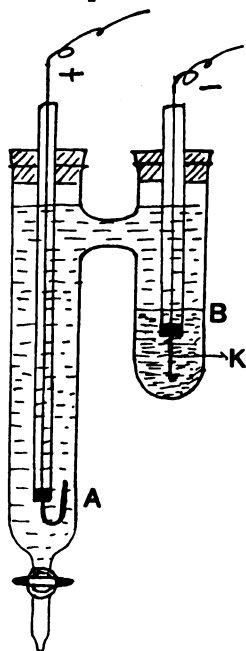


FIG. 48

Hittorf showed that the transport numbers are practically independent of the electromotive force between the electrodes. They are, however, influenced by temperature to some extent, and in the case of mono-atomic univalent ions approach 0.5 as the temperature rises.

Experiment to Determine the Transport Numbers of the Silver Ion and the Nitrate Ion in a Solution of Silver Nitrate—The apparatus which is best suited for this purpose is Ostwald's modification of Hittorf's apparatus (see Fig. 48): two glass tubes, usually of unequal length, connected near the upper end. The lower end of the shorter limb is closed, while the longer limb is provided with a stop-cock. Into the tubes are fitted, by means of paraffined corks, two electrodes. The one in the longer limb is of silver, made by fusing stout silver wire on to stout copper wire, and cementing the electrode into a glass tube so that only the silver is exposed.

The electrode in the shortest limb may be wholly of copper, but it should be enclosed partly in a glass tube. Prior to the experiment the silver anode should be coated with finely divided silver by electrolysis (see p. 128). The shorter limb, which is the anode compartment, is filled with a concentrated copper nitrate solution to just above the exposed part of the electrode. The rest of the apparatus is then carefully filled

with $\frac{n}{20}$ silver nitrate in such a way that a fairly sharp boundary is maintained between the copper nitrate solution. The cell is now connected in series, with variable resistance, an ammeter, a copper voltameter, and a source of current, such as an electric lighting circuit. The resistance must be so adjusted that a current of 0.01 ampère and a difference of potential of 30 to 40 volts is passed.

The copper voltameter may be made up in a glass cylinder as follows: Make up a solution of 125 grams, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 50 grams H_2SO_4 , 50 grams of alcohol, and a litre of water. Two copper electrodes of about 2 cms. square are cut from sheet copper. The cathode must be cleaned and weighed at the commencement, and then at the end of the experiment it is washed first with distilled water, and then with alcohol, dried, and again weighed. CO_2 should be passed through the voltameter during the experiment.

When the apparatus has been fitted up as indicated, the current is passed for about two to three hours. At the end of this time the cathode of the voltameter is removed, and weighed according to previous directions.

Then run off a measured volume of about three-quarters of the anode solution, weigh it, and determine the amount of silver present by titration with thiocyanate or electrolytic deposition. The remainder of the silver nitrate solution is then run off, and on analysis should have as near as possible the original composition. If not, the experiment must be repeated for a shorter period.

From the weight of copper deposit on the voltameter cathode and the change in silver concentration at the anode the transport numbers can be calculated as follows:

Calculation—Before the experiment: 15.06 grams of solution contained 0.127 gram of silver nitrate, which equals 0.000747 gram equivalents of silver for 15.06 grams of solution.

After the experiment: 20.28 grams of anode solution contained 0.2113 gram of silver nitrate, which equal 0.00124 gram equivalents of silver for 20.28 grams of anode solution.

Hence, before the experiment 14.933 grams of water contained 0.000747 gram equivalents of silver, after the experiment 20.0687 grams of water contained 0.00124 gram equivalents.

If there had been no change in composition, 20·0687 grams of water would have contained—

$$\frac{0\cdot000747 \times 20\cdot0687}{14\cdot933} = 0\cdot001004 \text{ gram equivalents of silver.}$$

So the increase was $0\cdot00124 - 0\cdot001004 = 0\cdot000236$ gram equivalents of silver. The weight of copper deposited in the copper voltameter was 0·0145 gram, or 0·0004602 gram, equivalents of copper. Hence the amount of silver liberated at the anode due to the discharge of NO_3 ions was 0·0004602 gram equivalents of silver, therefore the concentration ought to have increased by this amount if no silver had migrated to the cathode. The amount which must have migrated equals—

$$0\cdot0004602 - 0\cdot000236 = 0\cdot0002242 \text{ gram equivalents.}$$

Now, the values 0·000236 and 0·0002242 must be proportional to the velocities of anion and cation respectively.

Hence the transport number for silver ion equals

$$1 - n = \frac{0\cdot0002242}{0\cdot0004602} = 0\cdot487,$$

and for NO_3 ion—

$$n = \frac{0\cdot000236}{0\cdot0004602} = 0\cdot513.$$

CHAPTER XIV

ELECTRICAL CONDUCTIVITY

ELECTRICITY may be conveyed in two ways: (1) By conductors in which there is no transference of matter, as in the case of metallic conductors; (2) by conductors which undergo simultaneous decomposition, as in the case of fused salts and solutions.

In the present case we are only concerned with the second type of conductor.

Ohm's Law, which holds for conductivity in general, may be stated somewhat as follows: *The strength of an electric current passing through a conductor is proportional to the difference of potential between the two ends of the conductor, and inversely proportional to the resistance of the latter—i.e.,*

$$\text{current} = \frac{\text{difference of potential}}{\text{resistance}}, \text{ or ampères} = \frac{\text{volts}}{\text{ohms}}.$$

This is usually expressed symbolically thus :

$$C = \frac{E}{R}.$$

The standard of resistance is 1 *ohm*, and is defined as the resistance of a column of mercury 106.3 cms. long, and weighing 14.4521 grams, and the resistance measured at 0°.

An *ampère* is that strength of current which will deposit 0.001118 gram of silver from a solution of silver nitrate, under definite conditions, in one second.

The quantity of electricity which passes in one second with current strength of 1 ampère is known as a *coulomb*.

When a current of 1 ampère passes along a conductor whose resistance is 1 ohm, then the difference of potential between the two ends of the conductor is 1 *volt*.

The unit of electrical energy is 1 volt $\times$ 1 coulomb, and is equal to 10^7 ergs.

The resistance of a conductor is proportional to its length and inversely proportional to its cross section. Hence the resistance R is given by equation $R = \rho \frac{l}{s}$ where ρ is a constant. If l and s are each unity, then $R = \rho$. The constant ρ is known as the *specific resistance*, and may therefore be defined as the resistance in ohms offered by a cube of 1 cm. dimensions to a current of electricity. It will be seen that a conductor of low resistance will have a high conductivity. Hence *specific conductivity* will be the inverse of specific resistance, and therefore equal to $\frac{1}{\rho} = \kappa$, where κ is the specific conductivity.

Specific conductivity is measured in *reciprocal ohms*, frequently termed "mhos."

In dealing with solutions, the conductivity does not depend upon the solvent, but on the solute, and it is convenient to compare solutions containing quantities of solute proportional to the respective molecular weights.

By *molecular conductivity* is meant the conductivity or conductance of a solution containing 1 gram molecule of solute when placed between electrodes of indefinite dimensions exactly 1 cm. apart, and is represented by μ .

$$\mu = \kappa V, \wedge$$

where V is the volume in cubic centimetres, which contains 1 gram molecule of solute.

By *equivalent conductivity* is meant the conductivity of a solution which contains 1 gram equivalent of solute, when placed between two electrodes 1 cm. apart. It is usually represented by Λ

$$\Lambda = \kappa V,$$

where V is the volume, which contains 1 gram equivalent of solute.

It will be seen that for such substances as KCl, which gives rise to two simple monovalent ions, $\mu = \Lambda$.

Determination of the Conductivity of Electrolytes—The great difficulty in determining electrical conductivities lies in the fact that by the use of a continuous current the products of

electrolysis accumulate at the two poles and set up a back electromotive force of uncertain value. This effect is known as *polarization*. The actual resistance measured will be therefore the sum of the resistance of the solution and the polarization at the electrodes. This difficulty was overcome by Kohlrausch, who proposed the use of an alternating current instead of a direct current. By this means the polarization caused by the passage of the current in one direction is removed before it has time to attain any appreciable magni-

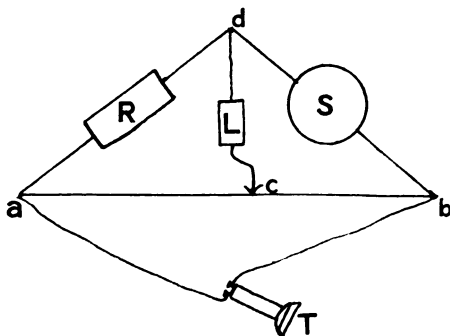


FIG. 49

tude by the reversal of the current and its passage in the opposite direction. Hence by this means the true resistance, and hence the conductivity of the electrolyte, can be determined.

The most suitable mode of obtaining an alternating current in the present case is by means of a small induction coil.

The method usually employed to determine the resistance of an electrolyte is the Wheatstone bridge method. The arrangement of the apparatus is shown diagrammatically in Fig. 49.

R is a known resistance, S the cell with platinum electrodes, between which the resistance of the solution is to be measured; $a-b$ is a platinum wire (may be iridium-platinum or nickelin) of uniform thickness, which is usually about a metre long, and is stretched along a scale graduated in millimetres; C is sliding contact. By means of a battery a direct current is sent through the coil L , thereby giving rise to an alternating current

which divides into two circuits at the contact C , one part going along the circuit C, a, d through R , and the other along C, b, d through the cells S . The object of the experiment is to balance these two circuits. This is done by means of a sliding contact at C . Since an alternating current is used, a galvanometer cannot be used, so a telephone T is connected to $a-b$. The sliding contact C is moved along the wire until there is

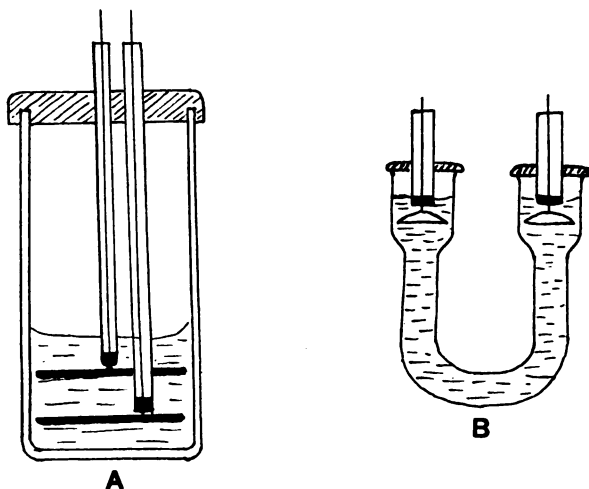


FIG. 50

no sound in the telephone. When this is the case, a balance has been made between the two circuits, hence the points a and b must be at the same potential. When such circumstances exist, the following relationship holds—

$$R : S :: a-c : c-b ;$$

$$\text{i.e., } S = R \frac{cb}{ac}.$$

Here R is known, as cb and ac can be measured. Hence the resistance of the cell S can be easily calculated.

In actual experiment it is not usually possible to obtain complete silence in the telephone, so the point of minimum

sound is taken—*i.e.*, a point such that if the contact be moved, the least bit either to the left or to the right the intensity of the sound is increased. The coil used in these experiments should be as small as possible, so that the amount of current which passes at each pulse is as small as possible. The coil may be worked from a small accumulator or dry cell, but the current should be regulated with a sliding resistance, so that the sound of the coil can be distinctly heard, the vibration of the hammer being quite uniform. The resistance usually takes the form of the ordinary type of resistance box, the various resistances being put in circuit by the removal of brass plugs, thereby causing the current to pass through a wire of definite resistance; the value of each resistance being indicated on the box.

Various types of *electrolytic cell* are used. Fig. 50 indicates two types. *A* is a type used for solutions of small conductivity while *B* is used for solutions of high conductivity. The electrodes are circular platinum plates fitted with platinum wires, which are sealed into glass tubes. These tubes are held in position by being fixed into the ebonite cover which closes the cell. The electrical contact is made by placing mercury in the tubes. The open ends of the glass tubes attached to the electrodes should be closed by rubber plugs when the apparatus is not in use. The *bridge*, which is represented by

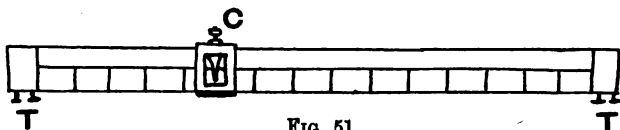


FIG. 51

ab in Fig. 49, is seen in detail in Fig. 51. The ends of the wire are frequently held in position by the brass plates, and to each of these brass plates two terminals are fixed. *C* indicates the platinum contact, which also carries a connecting terminal.

It will be seen that the actual length of wire necessary in bridge form will depend upon the ratio $\frac{R}{S}$. The nearer this is to unity, the nearer to the centre of the scale will be the final position of *C*. So that if *R*, *S* are suitably arranged, the

position of C may be confined to about 40 or 50 cms. in the centre of the scale. Hence the actual bridge can be reduced in length, and the excess of wire wound round a suitable drum.

In some special forms of apparatus modifications of this type are introduced, and in some cases the scale is so graduated to give directly the ratio of the two resistances (see Fig. 52).

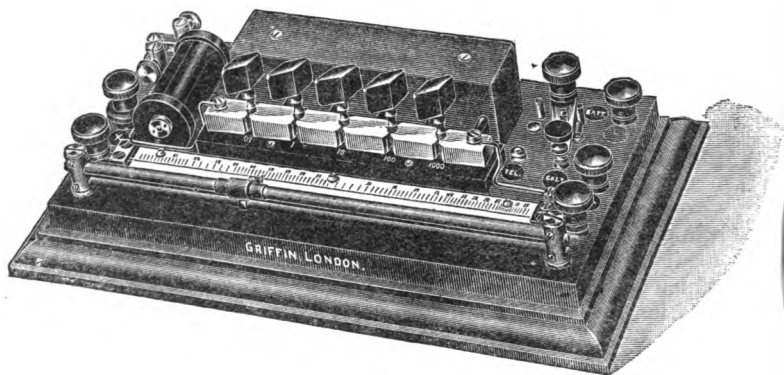


FIG. 52

It is not advisable to rely upon the accuracy of the bridge scale, as the wire is rarely absolutely uniform. The motion of the contact over the wire also changes its resistance slightly; so it is necessary to calibrate the wire from time to time.

Calibration of the Bridge Wire—The difficulty of measuring the resistance of short lengths of the wire lies in the uncertainty of making a contact with other wires which shall be free from resistance. The method usually adopted is that devised by Strouhal and Barus, which is based on the Wheatstone bridge principle. In this method the resistances of the contact do not interfere with the measurement. Ten approximately equal resistances are required, the sum of which should be about the same resistance as that of the bridge wire. These resistances are in the form of wire coils (Fig. 53) soldered on to stout copper wire, and for protection they are mounted in glass tubes. The ends of the copper wire are thoroughly cleaned and amalgamated, and arranged along a

board, as shown in Fig. 54, the ends of the copper wires dipping into cups filled with mercury, thus connecting up the series. This is then placed parallel to the bridge to be

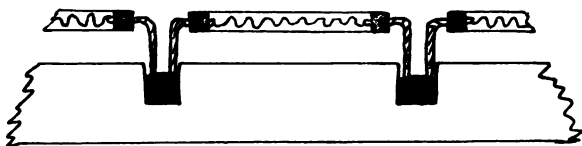


FIG. 53

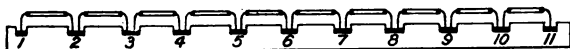


FIG. 54

tested. The principle of the method is to find lengths of wires at different positions along the bridge which are of equal resistance. The source of current in this case may be either direct or alternating, the exact compensation being

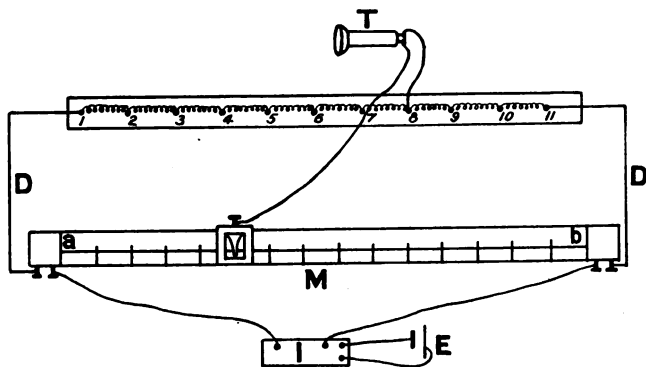


FIG. 55

detected by a sensitive galvanometer in the former case, and by a telephone in the latter case.

The bridge is then connected to the resistance series by stout copper leads, *D*. The whole arrangement will be understood from Fig. 55. One of the resistance coils must be

chosen as a standard, and should carry some suitable mark of distinction. It does not matter which of the coils is chosen as the standard. The *standard* coil is placed in cups 1 and 2, and one of the wires from the telephone placed in cup 2 (see Fig. 55); then the point on the bridge wire, where a balance is noted. Now move the standard coil to position 3 without changing the telephone wire, and again determine the balance-point. The telephone wire is now placed in cup 3, and re-determine the balance. The difference between the last two readings corresponds to a length of the bridge wire, the resistance of which is the same fraction of the total resistance of the bridge wire as the standard is of the sum of the ten resistance coils.

The "standard" is now brought to position 3, 4, the telephone wire being first in 3, and then in 4, and the balance determined in each case. This is repeated until the standard has reached position 10, 11, where only one reading is taken—*i.e.*, with the telephone wire in cup 10. By this method the bridge wire has been divided up into ten equal resistances, each of which is equal, or approximately equal, to one-tenth of the whole resistance. These ten lengths are added together, and the *difference* of the sum from 1000 mm. divided by 10, and each single value corrected by this amount, so that now the sum is exactly 1000 mm.—*i.e.*, the exact length of the bridge wire, which, of course, it must be equal to.

If the single corrected values are now added together as follows, 1, 1 + 2, 1 + 2 + 3, and so on, we obtain readings which correspond to successive tenths of the wires.

This will be better understood by studying the example on p. 99, which is derived from an actual experiment.

It is advisable to plot a graph from values in the sixth column of figures, so that any intermediate values may be approximately determined.

Purity of the Water used for Conductivities—It is absolutely essential that water used in conductivity experiments, owing to the sensitiveness of the method of experiment, be of a high degree of purity.

Water exhibits very different degrees of conductivity, depending upon the manner of distillation and preservation; while perfectly pure, freshly distilled water exhibits an extremely low conductivity.

The purest water so far obtained had a specific conductivity

Position of Sliding Contact corresponding to the End of Standard Coil at—		Lengths of Equal Resistance	Difference Correction	Corrected Lengths of Equal Resistance	Sum of Equal Resistances Corresponding to 100, 200, and 300 on the Bridge	Correction at End-Points
Left Hand	Right Hand					
Mm.	Mm.					
Terminal	97·8	97·8	- 0·19	97·61	97·61	+ 2·39
98·7	200·1	101·4	- 0·19	101·21	198·82	+ 1·18
199·6	301·4	101·8	- 0·19	101·61	300·43	- 0·43
301·3	400·8	99·5	- 0·19	99·31	399·74	+ 0·26
401·1	502·1	101·0	- 0·19	100·81	500·55	- 0·55
500·9	601·5	100·6	- 0·19	100·41	600·96	- 0·96
600·4	700·9	100·5	- 0·19	100·31	701·27	- 1·27
700·1	800·3	100·2	- 0·19	100·01	801·28	- 1·28
800·4	399·7	99·3	- 0·19	99·11	900·39	- 0·39
800·2	Terminal	99·8	- 0·19	99·61	1000·00	—
Sum of lengths of equal resistance		= 1001·9		1000·00		

Note—The positive values in Column 7 are the values to be added to Column 6 in order to give the actual bridge reading, the negative values being subtracted. Hence the positive are subtracted and the negative added to the actual bridge reading to give the *corrected reading*.

of 0.04×10^{-6} reciprocal ohms at 18° , but water with a conductivity up to 3×10^{-6} reciprocal ohms can be used for experiments, in which a fair degree of accuracy is required.

The chief causes of conductivity are the presence of small quantities of carbon dioxide and ammonia.

The ordinary laboratory distilled water is frequently sufficiently pure for ordinary purposes. It can be considerably improved by redistillation in as pure an atmosphere as possible, neglecting the first and last fractions.

Where a high degree of purity is required, the condenser should, according to Kohlrausch, be of block tin, but frequently a Jena glass tube in the condenser is sufficient. The water should be preserved in a glass flask which has been used for a long time to contain distilled water. The flask should be closed with a paraffined cork fitted with siphon tube and soda-lime tube. If the water contains much carbon dioxide, it may be treated with baryta before distillation.

In cases where absolute accuracy is necessary, the conductivity of the water itself must be determined.

Determination of Cell Constant—The resistance of an electrolyte must depend on the *capacity of the cell*. By capacity is meant the actual volume of solution which is actually between the electrodes, or, in other words, upon the product of cross section of the electrodes and the distance between them. The specific conductivity, and hence the specific resistance, could be calculated if these two factors were known, but it is more convenient to determine what is termed the *cell constant*, which is proportional to its capacity. This is done by using an electrolyte of known conductivity, and a $\frac{1}{50}$ normal solution of potassium chloride is usually used for this purpose. As before mentioned (p. 94)—

$$S = \frac{Rcb}{ac}.$$

Hence conductivity—

$$C = \frac{1}{S} = \frac{ac}{Rcb}.$$

Therefore C can be determined by experiment.

Further, the specific conductivity κ must be proportional to the observed conductivity— $\kappa = KC$.

$$\therefore \frac{\kappa}{C} = K,$$

K being the cell constant.

Experiment to Determine the Cell Constant by Means of $\frac{n}{50}$ Potassium Chloride—The type of cell used in this experiment should be that with the electrodes near together (Fig. 50, A).

The experiment must be carried out in a thermostat at 25° . It is essential that the temperature of the thermostat should be exceedingly constant, since a change of 1° influences the result 2 per cent. The cell, thoroughly clean, is

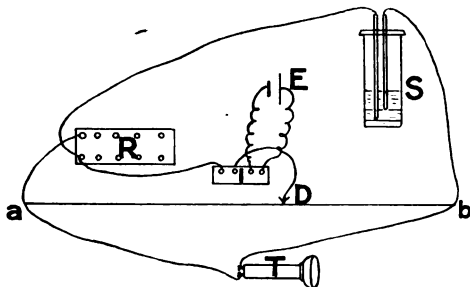


FIG. 56

supported in the thermostat and connected up by stout copper wire, of negligible resistance. The ends of the wire must be cleaned with emery paper so as to give a good contact. The ends of the wire which make a mercury contact (at the conductivity cell) should be amalgamated. The arrangement of the apparatus will be understood from Fig. 56.

The electrodes should be coated with a uniform layer of platinum black (see note at end of chapter), and when freshly platinized they contain traces of impurity which cannot readily be washed out, and which would increase the conductivity.

To remove this, put conductivity water into the cell to just above the electrodes and determine the resistance of the cell.

Any soluble matter entrained in the platinum black will slowly dissolve out. Pour out the water from the cell, put in fresh, and again determine the resistance. Repeat this until the resistance is constant, or only differs by 3—4 mm. on the bridge. Note this last reading, because from it we can calculate the conductivity of the water when we have determined the cell constant. Make up carefully a $\frac{N}{50}$ solution of pure potassium chloride. Wash the electrodes once or twice with it. Then fill up the cell to just above the electrodes, and then allow the solution to come to the temperature of the bath. Then determine the resistance of the solution. The resistance put in from the box should be so arranged that the reading falls somewhere between 25 and 75 cms., because an error in the readings at either end of the bridge influences the result to a greater degree than a similar error about the middle of the wire. Having determined the position of minimum sound, change the resistance in the box and again determine the balance. Then empty the cell and fill up again with fresh solution and repeat the above proceedings. Calculate the cell constant as indicated below from each of the resistance readings, and take the mean value.

Given for KCl—

$$\begin{aligned}\kappa &= 2.768 \times 10^{-3} \text{ at } 25^{\circ}, \\ &= 2.399 \times 10^{-3} \text{ at } 18^{\circ}, \\ &= 1.996 \times 10^{-3} \text{ at } 10^{\circ},\end{aligned}$$

expressed in reciprocal ohms.

Let R be the resistance in the box, S the resistance of the cell, x the bridge reading in centimetres, then

$$\frac{100-x}{x} = \frac{S}{R} \quad \therefore S = \frac{R(100-x)}{x};$$

but

$$S = \frac{1}{C} \quad \therefore C = \frac{x}{R(100-x)}.$$

Again—

$$K = \frac{\kappa}{C} \text{ where } \kappa = \text{specific conductivity.}$$

$$\therefore K = \frac{\kappa(100-x)R}{x},$$

K being the cell constant.

Having obtained the cell constant, the conductivity of the conductivity water can be calculated, for the resistance of the cell containing the conductivity water has already been determined when testing the electrodes. The equation in—

$$K = \frac{\kappa(100 - x)R}{x},$$

κ is the only unknown, and hence can be easily calculated.

If any difficulty is experienced in obtaining a balance, it may be due to the fact that sufficient time has not elapsed for the cell to attain the temperature of the bath. If, however, after a reasonable interval the results are unsatisfactory, the electrodes should be replatinized.

The current should not be allowed to pass through the cell for any considerable period, as this tends to heat up the cell.

Determination of Molecular Conductivity and Degree of Ionization—If κ is the specific conductivity of a solution of known concentration, then the molecular conductivity is given by $\mu_v = \kappa V$, V being the volume which contains 1 gram molecule of solute. If κ be determined for a whole series of dilutions of the original solution, the value of μ will finally approximate to μ_∞ —i.e., molecular conductivity at infinite dilution.

It is, however, not possible to measure the conductivity at infinite dilution with any degree of accuracy, so use is made of Kohlrausch's law, which states that the molecular conductivity at infinite dilution is equal to the sum of the velocities of the ions—

$$\mu_\infty = (u + v),$$

where u and v are the speeds of the cation and anion respectively. At any given dilution V the formula will be—

$$\mu_v = a(u + v),$$

where a represents the fraction of the molecules of the solute, which is ionized. Hence we get, by dividing the second equation by the first—

$$a = \frac{\mu_v}{\mu_\infty};$$

that is, the degree of dissociation a at any dilution is the ratio of the molecular conductivity at that dilution to the molecular conductivity at infinite dilution.

Consider, say, the case of a solution of acetic acid of concentration 1, and let α represent the fraction which split up into ions. Then the concentration of the undissociated portion will be represented by $\frac{1-\alpha}{V}$, where V is the volume, and the concentration of *each* ion will be $\frac{\alpha}{V}$. Hence, by the law of mass action, we get—

$$\left(\frac{\alpha}{V}\right)^2 = k\left(\frac{1-\alpha}{V}\right);$$

or

$$k = \frac{\alpha^2}{(1-\alpha)V},$$

where k is the equilibrium constant.

Now, substituting $\frac{\mu_v}{\mu_\infty}$ for α , we get—

$$k = \frac{\mu_v^2}{\mu_\infty(\mu_\infty - \mu_v)V}.$$

k is known as the dissociation constant or ionization constant.

The above value is usually very small, so $K = 100k$ is usually quoted as the dissociation constant; μ_∞ cannot be found directly as a rule, but has to be calculated from the ionic velocities, as before indicated.

Experiment to Determine the Molecular Conductivity and Dissociation Constant of Succinic Acid—The apparatus in this case is the same as in the former experiment. The cell and electrodes must be clean and dry. The electrodes may be conveniently dried by washing first with distilled water and then with pure alcohol, and then allowed to dry in a warm atmosphere free from fumes.

Prepare $\frac{1}{16}$ molar solution of succinic acid, and place 20 c.c. (or other convenient *definite* quantity according to size of cell) of this solution in the cell, in the thermostat at 25°. When solution has taken the temperature of the bath, determine the resistance as in previous experiment, using three different resistances in the box. Now withdraw carefully 10 c.c. (if 20 c.c. has been used, otherwise half the original volume) of solution from the cell, and introduce 10 c.c. of conductivity water (from a stoppered flask which has been kept in the

thermostat). Mix the water and solution thoroughly, and then determine the resistance again. Repeat this process until the dilution reaches 1 gram molecule in 1024 litres—i.e., make six dilutions. The dilutions are as follows:

One gram molecule to 16, 32, 64, 128, 256, 512, 1024 litres.
Calculation—

$$K = \frac{\kappa(100-x)R}{x};$$

$$\kappa = \frac{K}{R} \frac{x}{(100-x)}.$$

Since $\mu_v = \kappa V$,

$$\mu_v = \frac{KV}{R} \frac{x}{(100-x)}.$$

Hence the molecular conductivity for various values of V can be calculated.

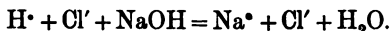
Again, substituting the values found for μ_v in equation—

$$k = \mu_\infty \frac{\mu_v^2}{(\mu_\infty - \mu_v)V};$$

given also that μ_∞ for succinic acid equal 381, k can be easily calculated, and also $K = 100k$, k being the dissociation constant.

The value k is a very important constant, since it is a measure of the strength or affinity of acids and bases. It is therefore frequently called the *affinity constant*.

Application of Conductivity Measurements to Determine Neutralization Points—Consider the case of a dilute solution of hydrochloric acid. According to Kohlrausch's law, the conductivity depends upon the sum velocities of the ions—in this case the chloride ion and the hydrogen ion. Now, suppose a little caustic soda is now added, part of the acid will be neutralized. This means that some of the hydrogen ions have been replaced by sodium ions—viz.:



Now, the velocity of the sodium ion is much less than that of the hydrogen ion. Hence the effect will be to reduce the conductivity. Further, the conductivity will decrease until the whole of the acid has been neutralized. As soon, however, as the neutralization is complete, further additions of caustic soda increase the number of ions—i.e., increase the

sodium ions and also introduce OH' ions, therefore the conductivity begins to rise again ; and since the OH' ion is very mobile, the turning-point is very decided.

Experiment to Determine the Strength of a Given Solution of Hydrochloric Acid—The manipulation is as in previous experiments. Introduce into the cell a known volume of hydrochloric acid (dilute) and determine the resistance as before. Run in from a burette small quantities of standard caustic soda, and determine the resistance at each point. At a certain point the direction of the movement of the sliding contact will change. Then the neutralization-point has been passed. Make three or four readings after this. To determine the exact neutralization-point plot the bridge readings as ordinates against the number of cubic centimetres of acid added. The point of intersection of the two curves thus obtained gives the exact point of neutralization.

This method is of value when dealing with highly coloured or turbid liquids. In the case of weak acids use a strong base, and add the acid to the base to obtain a decided break in the curve.

Note : Platinizing Electrodes—Thoroughly clean the electrode by means of chromic acid solution. Prepare also a 3 per cent. solution of chloroplatinic acid to which 0.025 gram of lead acetate is also added. Place the electrodes in the solution, and connect up to a 4-volt accumulator. A commutator, or a reversing switch must also be in the circuit. Pass the current for about fifteen minutes, reversing it every half-minute, so that each electrode becomes cathode and anode alternately. The evolution of the gas should not be too rapid. This may be controlled by having a sliding resistance in the circuit.

Owing to the horizontal position of the electrodes, the gas is very liable to collect underneath, thereby causing uneven distribution of the platinum black. This may be avoided by supporting the electrodes in an inclined position. When finished the electrodes should present a fine velvety appearance. They still contain a small amount of absorbed platinizing liquid and a small amount of chlorine. To get rid of this place the electrodes in dilute sulphuric acid, and pass the current for fifteen minutes, reversing it every minute.

Then wash the electrodes several times in warm distilled water, and then conductivity water, and finally preserve them in conductivity water required for use.

CHAPTER XV

MEASUREMENTS OF ELECTROMOTIVE FORCE

IN the present chapter we are concerned mainly with the study of the relation between chemical and electrical energy.

Electrical energy, it must be remembered, involves two factors, namely, *the amount of electricity* and *electromotive force*, or *fall in potential*. Of these two factors the latter, namely, electromotive force, is the more important, and will be considered in some detail in the succeeding pages.

When a chemical reaction takes place, the energy of the reaction, or chemical affinity, may manifest itself in the form of heat. Hence heat of reaction is frequently used as a measure of affinity. Many reactions, on the other hand, give rise to electrical energy, as in galvanic cells; in these cases a measure of chemical affinity can be obtained from a measurement of electromotive force. It must not be assumed from this that electromotive force is equal to the heat of reaction, or that electromotive force is a measure of the heat of reaction. In some cases they are equal, but generally they are not equal. The electromotive force is rather a measure of the diminution of *free energy* of a system.

The relation between free or available energy and the heat of reaction in a *reversible reaction* given by the thermodynamical equation—

$$A - U = Q,$$

where A is the free energy—i.e., that portion of the energy which can be transformed into work— U is the diminution of the total energy of the system (diminution of internal energy), and Q is the heat of the reaction.

This equation may be written as a free energy equation—

$$A - U = T \frac{dA}{dT}.$$

When, however, the chemical energy of the reaction is transformed into electrical energy, it is only necessary to substitute the corresponding electrical terms in the above equation to get an expression of the relationship between the chemical energy transformed and the maximum electrical energy obtainable in a *reversible* galvanic element. The resulting equation is—

$$nFE - Q = nFT \frac{dE}{dT};$$

or

$$E = \frac{Q}{nF} + T \frac{dE}{dT}.$$

Where E is the E.M.F. of the cell, Q is the heat of reaction; for *molar* quantities, expressed in electrical units, F is 96540 coulombs. T is the absolute temperature at which the cell is working, n is the valency or the number of charges carried by a molecule of substance undergoing change, $\frac{dE}{dT}$ is the temperature coefficient of the E.M.F. Q has been substituted for U , since they are equal when no external work is done. A becomes nFE —i.e., the maximum electrical energy for molar quantities— $\frac{dA}{dT}$ becomes $nF \frac{dE}{dT}$, n and F being constants.

The equation given above is known as *Helmholtz* equation.

On considering the equation in the first form, it will be seen that—

(a) If $\frac{dE}{dT}$ is positive, then $nFE > Q$, hence the cell takes heat from its surroundings while working.

(b) If, on the other hand, $\frac{dE}{dT}$ is negative, the $Q > nFE$, hence the cell becomes heated while working.

(c) If $\frac{dE}{dT}$ is zero, then $Q = nFE$ —i.e., the heat of reaction is equal to the electrical energy, and hence the temperature of the cell remains unaltered.

Measurement of Electromotive Force—The most convenient method of measuring the E.M.F. of a cell is by what is known as Poggendorff's compensation method. The principle of the method is that the E.M.F. of the cell to be tested is

just compensated by the E.M.F. of another cell in the opposite direction, the E.M.F. of the latter being adjusted so as to just balance the cell.

The general arrangement of the apparatus is shown in Fig. 57. *A* is a source of electricity of constant E.M.F., such as, say, a lead accumulator, which is connected by two copper wires to the ends of the uniform resistance wire, *B—C*, which may conveniently be a metre in length. The cell, *E*, the E.M.F. of which is required, is connected through some suitable measuring instrument, such as an electrometer or

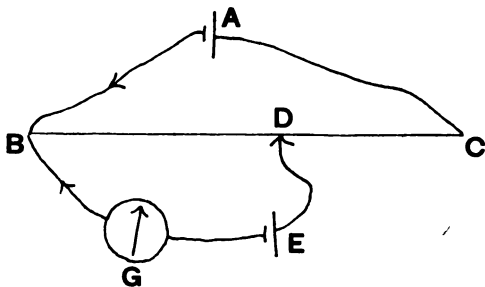


FIG. 57

galvanometer, *G*, and a tapping key to one end of the wire bridge at *B*, the other pole being connected to sliding contact *D*.

The point of balance is found by moving the sliding contact *D* to a position such as that when the contact is made through the tapping key no current passes through the galvanometer—*i.e.*, there is no deflection. When such conditions hold, we have the following relationship:

$$\text{E.M.F. of accumulator} : \text{E.M.F. of cell} :: \text{length } B-C : \text{length } B-D-$$

$$\therefore \text{E.M.F. of cell} = \text{E.M.F. of accumulator} \times \frac{B-D}{B-C}$$

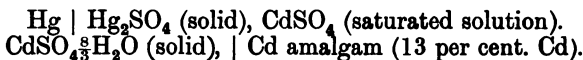
The E.M.F. of *A*, or, as it is called, the working cell, is not sufficiently constant for accurate experiments, so it is usual to do a preliminary determination with a standard cell—*i.e.*, a cell of known constant E.M.F. in place of *E*. Suppose we

find that the standard cell balances at D' , and the cell to be tested at D , then we have—

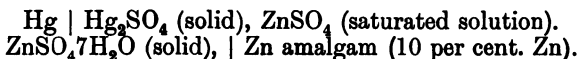
$$\frac{B-D'}{B-D} = \frac{\text{E.M.F. of standard cell}}{\text{unknown E.M.F. of cell } E}$$

It is essential that the E.M.F. of the working cell A should be greater than that of the cell whose E.M.F. is to be determined. Usually a 2-volt accumulator of large capacity, 30 to 40 ampère hours, will be found to meet the requirements. The measuring wire $B-C$ is usually the same as described for conductivity experiments (p. 95), and it should be calibrated in the same manner. If in a metre wire the difference of potential between the two ends is 2 volts, then 1 mm. on the bridge will correspond to 2 millivolts. So that it is easily possible to get a degree of accuracy of less than 1 millivolt of error with a fairly sensitive galvanometer.

The Standard of Electromotive Force—The standard usually employed is the *Weston cell*, the composition of which may be indicated as follows:



Another well-known standard is known as the *Clark cell*. This cell has the following composition:



The Weston cell is most frequently used now; it has the advantage of being easily reproduced, and has a very low temperature coefficient.

The cell itself usually consists of an **H**-shaped glass vessel.

The vertical tubes are sealed at the bottom (see Fig 58).

Into one of the limbs pour a layer of freshly distilled and thoroughly purified mercury to a depth of about 1 cm. Then prepare a paste of mercurous sulphate thus: Grind together in a mortar mercurous sulphate, a little mercury, and one or two crystals of cadmium sulphate, with a little saturated solution of cadmium sulphate. Filter through a plug of cotton-wool. Then rub the paste again with a little cadmium sulphate solution, and again filter. Repeat this process a third time. The object of this process is to completely remove any

traces of mercuric sulphate. Place the paste moistened with cadmium sulphate solution thus prepared to a depth of about 3 mm. over the mercury; then add several large clear crystals of cadmium sulphate. Into the other limb place a layer of cadmium amalgam prepared as follows: Heat at 100° (say on a water-bath) 7.5 parts by weight of pure mercury and 1 part of cadmium. Stir well with a glass rod. Heat up the limb of the cell in hot water, and add the liquid amalgam to a depth of about 1 cm., then allow to cool, and the amalgam solidifies. On the top of this amalgam place about

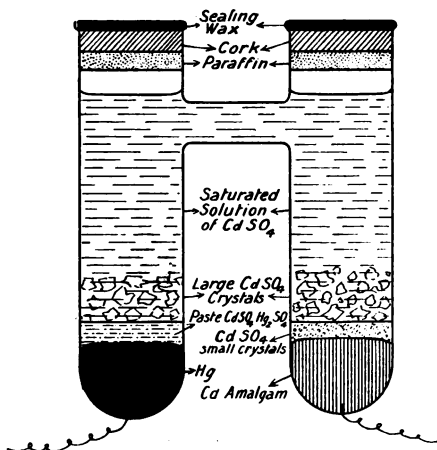


FIG. 58

3 mm. layer of finely powdered cadmium sulphate crystals, slightly moistened. Then add several large clear crystals of cadmium sulphate, and, finally, fill up the apparatus within about 1.5 cms. of the top with a saturated solution of cadmium sulphate. The cadmium sulphate crystals used in making up the above cell must have the composition $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$, and in preparing a saturated solution of the salt the temperature should be kept below 75° , because above this temperature the monohydrate is the stable phase—i.e., $\text{CdSO}_4 \cdot \text{H}_2\text{O}$.

The open ends of the tube must now be hermetically sealed, at the same time an air space must be left in the tubes for

expansion due to rise in temperature. A small quantity of clean paraffin wax is melted, the cell tilted a little to the left, and the paraffin wax poured carefully on to the surface of the solution in the left-hand limb to a depth of about 0.5 cm. The tube is then tilted to the right, and the right-hand tube treated in the same way. On the top of the paraffin place a layer of cork 0.5 cm. thick, and, finally, close the tube with the sealing wax. In the above cell the mercury is the positive pole, and the amalgam the negative pole. The E.M.F. of the *Normal Weston cell* is practically independent of temperature, as it only changes -0.00004 volt per degree for the range 15° to 20° .

THE E.M.F. AT TEMPERATURES FROM 0° TO 30°

Temperature	E.M.F. in Volts
0°	1.0189
5°	1.0189
10°	1.0189
15°	1.0188
20°	1.0186
25°	1.0184
30°	1.0181

Generally for a temperature t° .
 $E_t = 1.0186 - 0.00004 (t^{\circ} - 20)$ nearly.

For ordinary room temperatures we may take the E.M.F. as 1.019 volts. Care must be taken not to short circuit the cell, as this changes slightly the E.M.F., since it causes some solid Hg_2SO_4 to go into solution, and it takes some time for the cell to recover its normal condition. It is also advisable to enclose the cell in an opaque case.

The *Clark cell* only differs from the Weston in that zinc is substituted for cadmium in each case.

The temperature coefficient of the Clark cell is higher than that of the Weston, as will be seen from the following equation, which gives the value of the E.M.F. at any temperature (t°):

$$E_t = 1.433 - 0.0012 (t^{\circ} - 15^{\circ}) \text{ very nearly.}$$

In the experimental determination of E.M.F. it is found

much more convenient to use a *capillary electrometer* instead of a galvanometer.

Capillary Electrometer—The most convenient form of electrometer for common use is what is known as the open form of capillary electrometer, a useful design of which is indicated in Fig. 59. It consists of two fairly wide-bored tubes, one having a bulb at one extremity; these two tubes are joined together by a fine capillary tube. Pure, clean, dry mercury is poured into limb *A* until the mercury stands just over halfway up the fine capillary tube; then the bulb of limb *B* is filled to about halfway with mercury; the rest of the tube *B* is filled with dilute sulphuric acid (1 part sulphuric acid to 6 parts of water), which had been previously agitated with a little pure mercury. The sulphuric acid should make a clean junction with the mercury in the capillary. To do this blow down tube *A* until a little mercury has been drawn over into *B*. On releasing the pressure, the sulphuric acid will be drawn back into the capillary. It is sometimes necessary to suck at tube *A* in order to bring the sulphuric acid back, but care must be taken not to get the sulphuric acid round the bend. A platinum wire passes down tube *B*, making contact with the mercury; the wire is insulated from the sulphuric acid by means of a glass tube. Contact is made in limb *A* by means of a piece of platinum wire.

It is essential that in using the capillary electrometer the sulphuric acid limb should be connected with the positive pole, and the mercury limb with the negative pole. If they are connected in the reverse way—i.e., the mercury limb made the anode—the mercury would go into solution, giving rise to mercurous sulphate in the capillary, which would dirty the tube, thereby causing the mercury to stick

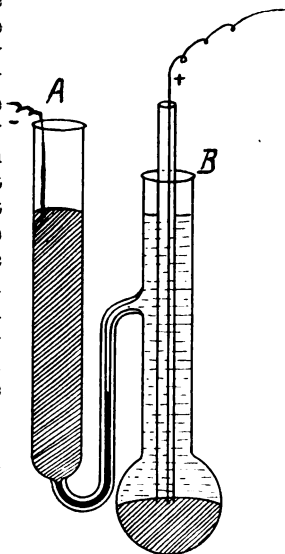


FIG. 59

and give fallacious results. If this should happen by accident, and another electrometer is not available, it should be thoroughly cleaned out with a hot solution of potassium bichromate and sulphuric acid, followed by several washings with distilled water, and finally dried with filtered air. It may then be filled as before described.

Principle of the Capillary Electrometer—When mercury and sulphuric acid in a capillary tube are connected in the manner mentioned above with some source of electromotive force, the area of separation between the liquids in the capillary diminishes. This is due to a *change* in the potential difference between the two liquids.

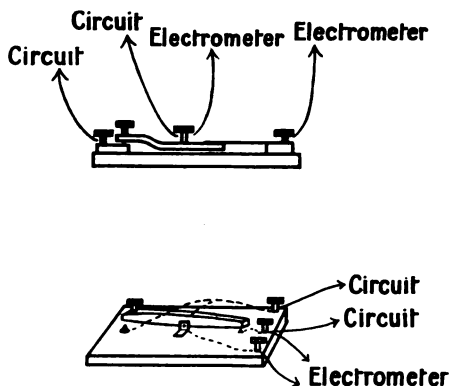


FIG. 60

A certain amount of mercury dissolves in the sulphuric acid, giving rise to mercurous sulphate. Now, the osmotic pressure of the solution of mercury salt will be greater than the solution pressure of the mercury, hence positive mercury ions from the solution will be deposited on the surface of the mercury, and this surface will, as the result of this, become positively charged with regard to the solution; then in all probability this positively charged surface holds a corresponding negative layer near the surface of the acid, thus giving a sort of Helmholtz double layer.

Another factor has also to be considered—namely, *surface tension*. The effect of surface tension is to tend to make the

surface area as small as possible. The attraction between the two oppositely charged layers will tend to counteract this effect; in other words, diminishes the surface tension.

In actual experiment the two poles of the electrometer must be connected so as to bring the two surfaces to the same potential difference before any measurement is made. This is achieved by means of a triple contact Morse key (Fig. 60). Now, if any increase or decrease charge be brought about from outside sources, then the concentration of the ions in the immediate neighbourhood of the mercury alters by causing some mercury to either pass into solution or else be deposited. The effect of this is to alter the potential difference, and hence the surface tension, thereby causing the mercury thread to rise or fall in the capillary tube; therefore when, on putting the electrometer into circuit, no movement occurs in the capillary tube, there is no difference of potential —i.e., both sides balance.

This form of electrometer was devised by *Lippman*, and is therefore known as *Lippman's Electrometer*.

The advantages of this electrometer consists in its action being practically astatic one, no current being taken from the element operating it.

In any experiment the object is, of course, to find the point at which the level of the mercury remains stationary, for then the two opposing potentials balance. If a high degree of accuracy is required, it is necessary to observe the meniscus of the mercury by means of a microscope, because, for small differences of potential, the meniscus alters only very slightly,

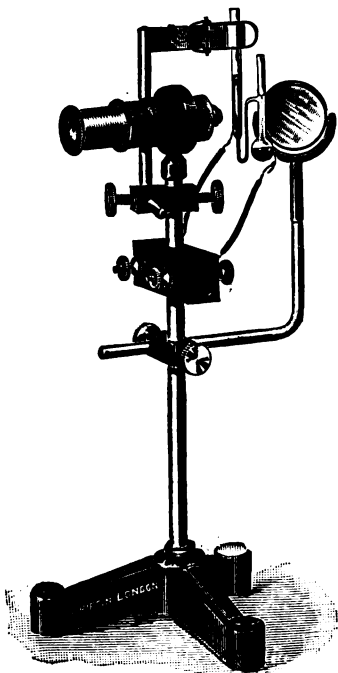


FIG. 61

and cannot be accurately observed with the naked eye. The electrometer and microscope are mounted on a suitable stand ; the electrometer should be illuminated by a mirror or diffused light from a suitably protected electric lamp. The apparatus is usually sold complete by the makers (see Fig. 61). The eyepiece contains a graduated scale, by means of which the rise and fall of the meniscus can be measured. With the aid of a microscope, the electrometer is sufficiently accurate to detect 0.0001 of a volt.

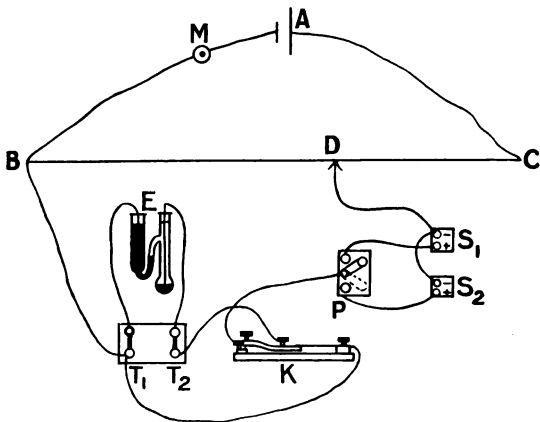


FIG. 62

Experiment Standardization of Weston Cell—The Weston cell, prepared according to the directions already given, must be compared with some other known standard cell. The apparatus is fitted up as shown in Fig. 62. *A* is the working cell connected to the end of bridge wire *B—C*; *E* a capillary electrometer; *T*₁, *T*₂ are connecting terminals; *K* is a Morse tapping key; *S*₁ is the known standard, and *S*₂ the standard to be tested, they are put in circuit separately, as required, by means of a two-switch, *P*; *D* is the sliding contact on the wire bridge. It is also advisable to insert a plug, *M*, so that the accumulator can be easily disconnected.

Make sure all connections are clean, and give a good contact; then put in circuit the known standard *S*₁; allow the

current to flow along the bridge wire by inserting plug M ; move the sliding contact to just past the middle of the bridge; press down the Morse key sharply, and observe through the microscope the movement of the mercury meniscus in the electrometer.

If the mercury appears to go down in the microscope—*i.e.*, in reality it moves up—then move the sliding contact down a little until a point is found where the mercury begins to move in the opposite direction. The *null-point* of the electrometer is between these two readings. Now move the sliding contact a few millimetres at a time until the motion of the mercury meniscus is again reversed. Repeat this process until a point is found such that a slight movement of the sliding contact either one way or the other causes the meniscus to move in the opposite direction. At the point itself the meniscus should not move at all on pressing the tapping key. As a check on the above result, find two points 1 mm. apart such that they give opposite directions to the motion of the meniscus; then measure the extent of the movement at both points by means of the scale in the eyepiece, and calculate the exact position of the balance by proportion. As the point of balance is approached, it will be necessary to keep the Morse key depressed several seconds before any movement may be detected. Now, having determined the balance-point for S_1 , alter the two-way switch so as to put S_2 in circuit instead of S_1 , and repeat the above process.

Then, if $B-D$ be the reading for S_1 , and $B-D_1$ for S_2 , we have—

$$\frac{\text{E.M.F. of } S_1}{\text{E.M.F. of } S_2} = \frac{B-D}{B-D'}$$

or

$$\text{E.M.F. of } S_2 = \text{E.M.F. of } S_1 \times \frac{B-D'}{B-D}$$

Measurement of Single Potential Differences—When a metal is dipped into a liquid, it possesses a certain definite solution pressure, so that the metal tends to dissolve; it can, however, only dissolve in the ionic form, hence it sends into solution a number of positively charged ions. The solution therefore becomes positively charged, and the metal must acquire the corresponding negative charge. An electric double layer is then found, and a state of equilibrium is ultimately

reached, when the electrostatic action of the double layer just balances the solution pressure of the metal. If, however, the liquid contains already a dissolved salt of the metal, the solution will already contain positive ions of the metal, and these positively charged ions will resist, by virtue of their osmotic pressure, any increase of metallic ions by solution of the metal. In this way a potential difference is set up between the metal and the solution, which will be equal to the difference between the solution pressure of the metal and the osmotic pressure of the ions in the solution. It will be clear that the relative charges on the metal and solution will depend on the relative values of the solution pressure of the metal and the osmotic pressure of the ions in solution.

Let P be the solution pressure of the metal, and p the osmotic pressure of the ions in the solution. Then, if—
(a) $P > p$, the metal sends ions into the solution until a balance is obtained; the metal will then be negatively charged and the solution positively charged.

(b) $P < p$ positive ions from the solution will be deposited on the metal until the electrostatic attraction balances the osmotic pressure, thus the metal will be positively charged and the solution negatively charged.

(c) $P = p$. In this case no change occurs, and no difference of potential between the metal and solution results.

The alkali metals (iron, zinc, etc.) belong to case (a), and mercury, silver, copper, etc., belong to case (b).

The amount of the charge can be calculated by considering the maximum work which is obtainable when a molecule of the metal at a solution pressure P passes into ions of osmotic pressure p .

On the assumption that the changes at the junction of metal and solution are reversible, then we have the osmotic work—

$$A = RT \log_e \frac{P}{p};$$

but $A = nFE$, where n is the valency of the metal, and $F = 96540$ coulombs.

$$\therefore nFE = RT \log_e \frac{P}{p},$$

or

$$E = \frac{RT}{nF} \log_e \frac{P}{p}.$$

Now, $R = 1.99$ cal. and $1 \text{ volt coulomb} = 0.239 \text{ cal.}$

$\therefore R = 8.316$, expressed in electrical units. Reducing to ordinary logs by multiplying by 2.3026 , we get—

$$E = \frac{0.0001983}{n} T \log_{10} \frac{P}{p}.$$

At room-temperature (15° to 20°) the equation—

$$E = \frac{0.058}{n} \cdot \log_{10} \frac{P}{p}$$

is usually taken, and it should be remembered in that form.

The system, which consists of a metal dipping in a solution of one of its salts, is termed a *half-element*.

The measurement of the potential between the electrode and the solution can only be done by comparing it with another electrode and solution whose potential difference is known. The method is to fit up a cell one of the electrodes, of which is the standard electrode of known E.M.F., and the other, the electrode the E.M.F. of which is desired; then the unknown E.M.F. will be the difference between the E.M.F. of the cell and the E.M.F. of the standard half-element. The most suitable form of standard electrode is the *calomel half-element*, which will now be described.

Calomel Electrode — The apparatus may be somewhat as shown in Fig. 63. It consists of a glass tube about 3.5 cms. wide, fitted on one side with a short, straight tube, *D*, and on the other side, about halfway, is attached a tube, *C*, bent twice at right angles. The open end of tube *C* is drawn out so as to somewhat constrict the opening. The apparatus should be thoroughly

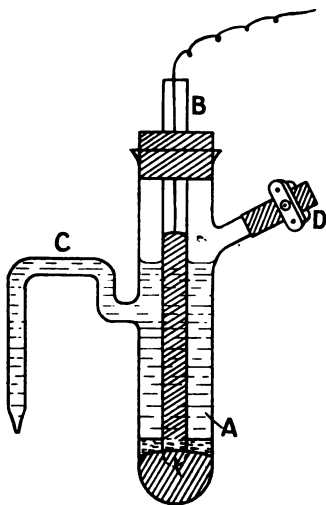


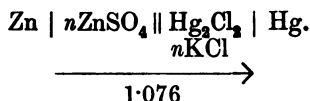
FIG. 63

cleaned with hot solution of potassium bichromate and sulphuric acid, and washed with distilled water several times, and then dried by directing a stream of hot filtered air into the tube; then about 2 c.c. of pure dry mercury are poured into the bottom of the tube. Prepare a normal solution of potassium chloride (pure recrystallized); then prepare a calomel paste as follows: Rub well together in a mortar calomel and pure mercury and a little of the potassium chloride solution, allow the mixture to settle, then decant off the solution; add a further portion of potassium chloride, and again work up the mixture in the mortar; once more decant off the solution. Repeat the above operation a third time; then add a portion of calomel paste thus prepared to the bulk of the potassium chloride solution, and shake the mixture in order to saturate the solution with calomel. Then decant off the clear solution for future use. Then with the remainder of calomel paste make a layer of 2 to 3 mm. over the mercury. Then fill up the tube to just about the point where tube *C* joins tube *A*. The connection with the mercury is made by means of a platinum wire sealed in a glass tube, *B*, the electrical connection being made by pouring a little mercury into the tube and inserting an amalgamated copper wire. The tube *B* is held in position by a paraffin cork, which closes the top of the cell. When a measurement is to be made, the side tube *C* must also be filled with the calomel-saturated potassium chloride solution. This is done by immersing the end of tube *C* in the solution and applying suction at *D* (to which a short rubber tube is attached), and, when *C* is completely full, closing *D* by means of a clip. The calomel electrode is termed the *absolute standard*, and has a potential difference of 0.560 volt at 18° between the mercury and the solution.

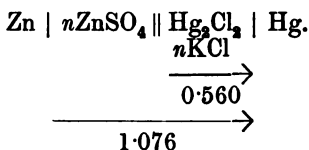
The great advantage of the calomel electrode as a standard is that it can be reproduced with a high degree of accuracy.

Use of Calomel Electrode to Determine Electrode Potentials—Suppose it is required to determine the potential difference between metal and solution when zinc is dipped into a normal solution of zinc sulphate, then the zinc electrode (see later, p. 122) is combined with the calomel electrode to form a cell. The E.M.F. of the cell is then determined by means of bridge wire, and is found to be 1.076 volts. Now, zinc is negative with respect to mercury, so that the current goes from zinc

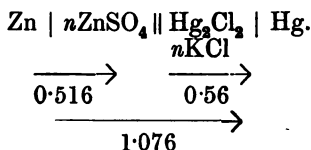
to mercury in the cell. This may be represented as follows :



We know, however, that positive electricity tends to pass from the solution to the mercury, and the difference of potential is 0.560 volt.



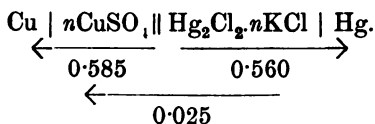
From this it is obvious that the potential difference between the zinc and the zinc sulphate must be 1.076 volts – 0.56 volt = 0.516 volt.



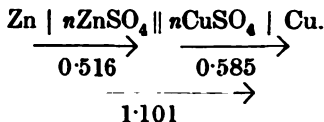
Consider cell :



Copper is positive with respect to mercury, hence the electricity flows from mercury to copper in the cell. The current in each electrode tends to flow from solution to the metal—i.e., in opposite directions—hence the E.M.F. of the cell will be the difference between the actual potentials of the two electrodes. The E.M.F. of the cell is 0.025 volt, hence Cu | nCuSO₄ junction the E M.F. is 0.585 volt.



From these two examples we see that the cell $\text{Zn} \mid n\text{ZnSO}_4 \parallel n\text{CuSO}_4 \mid \text{Cu}$ ought to have an E.M.F. of $0.516 + 0.585 = 1.101$ volts, this is in agreement with experimental fact.



Generally, the total E.M.F. of a cell is equal to the algebraic sum of potential differences of the two electrodes.

Preparation of $\text{Zn} \mid n\text{ZnSO}_4$ and $n\text{Cu} \mid \text{CuSO}_4$ Electrodes—
The glass portion of the electrode is identical with that described for the calomel electrode. Then pieces of pure zinc and copper rod about 3.5 cm. long are soldered to fine insulated copper wire. These are then mounted in glass tubes by means of sealing-wax or cement, so that the junction is not exposed—i.e., only the rod of pure metal projecting out of the tube to a length of 2.5 to 3 cm. It is now necessary to prepare the surfaces of these electrodes. In the case of zinc electrodes, they are first cleaned by dipping in dilute sulphuric acid and then the surface amalgamated by rubbing mercury over the surface with a piece of cotton-wool. Having got a uniform surface, the electrodes are then thoroughly washed with distilled water.

Copper electrodes must be coated with a fine deposit of electrolytic copper. First clean the surface of the copper by dipping in nitric acid, and then wash it with distilled water; then make up a copper solution, having the following constituents in the proportions indicated:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	...	...	125 grams
H_2SO_4	...	...	50 "
Alcohol	...	...	50 "
Water	...	...	1000 "

Then make the electrode the cathode and a strip of copper the anode; pass a current of density 0.5 ampères per 100 sq. cm. The electrode is thereby coated with a fine deposit of copper. If the current density used is too high, the deposit will be too coarse, and will not adhere properly. Two electrodes of each kind should be made, and each pair tested. The electrodes

then fitted into a paraffined cork; the tubes are filled with solutions of normal copper sulphate and normal zinc sulphate respectively. Now compare two zinc electrodes. Fit them as shown in Fig. 64; then fit up apparatus as used for testing standard cell (Fig. 62), substituting the above cell for S_1 , but connect the cell in series with S_2 , not in parallel, as before. Now, as before, determine the point of balance with the standard cell alone; then move the two-way switch so that both the cells are in circuit, and again determine the zero of both zinc electrodes are identical, then there should be no change in the zero. It frequently happens that there is a slight change in the zero—i.e., a slight E.M.F. in the

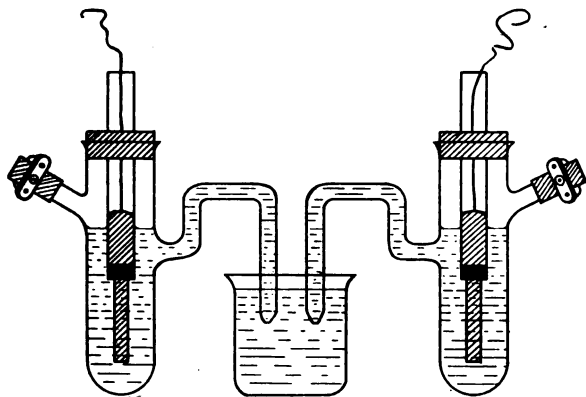


FIG. 64

$\text{Zn} \mid n\text{ZnSO}_4$ cell. This may be got rid of by joining up the two electrodes with a copper wire and short circuiting until there is no E.M.F. The copper electrodes should be tested in a similar manner.

Experiment: Determination of the Difference of Potential between Copper and a Normal Solution of Copper Sulphate— Prepare the $\text{Cu} \mid n\text{CuSO}_4$ electrode as previously described. Complete the cell by combining the copper electrode with a calomel electrode by means of three times normal potassium chloride (potassium chloride or nitrate solutions, fairly concentrated, and are frequently used to eliminate contact potential, which would result at the junction of the two liquids). Fit

up the apparatus as indicated in Fig. 65. E , the capillary electrometer, is connected up as previously described; S_1 is the Weston cell; S_2 the $\text{Cu} \mid n\text{CuSO}_4 \mid \text{KCl} \mid \text{Hg}_2\text{Cl}_2 \mid n\text{KCl} \mid \text{Hg}$ cell.

The cells S_1 and S_2 are connected in series. If a three-way key is available, it may be substituted with advantage for the two-way key indicated in previous experiments.

Now put the Weston cell only in the circuit, and determine the point of balance by moving the sliding contact D . Note

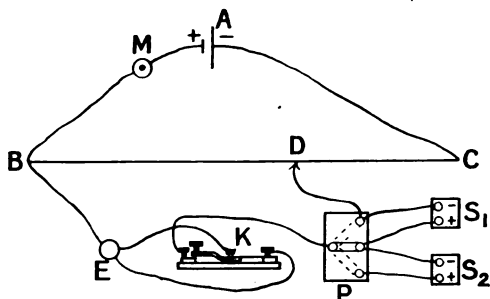


FIG. 65

the reading. Now put the unknown cell in circuit as well, and redetermine the point of balance. If, however, it is impossible to find a balance, no matter what the position of the contact D is, the wires attached to the unknown cell must be interchanged, since the above result was due to the positive pole of the cell being connected with the contact D . It will now be found possible to obtain a balance. Note the reading. The first reading corresponds to the E.M.F. of the Weston cell, and the second reading to the E.M.F. of Weston + the E.M.F. of S_2 . The readings will be proportional to the E.M.F.'s in the two cases—i.e.,

$$\frac{\text{E.M.F. of Weston} + S_2}{\text{E.M.F. of Weston}} = \frac{x_1}{x_2}$$

where x_1 is the reading for Weston + S_2 and x_2 for Weston alone.

Now, the E.M.F. of the Weston has been already found, say, 1.019 volts; hence we get—

$$\text{E.M.F. of } S_2 = \left(\frac{x_1}{x_2} \times 1.019 \right) - 1.019.$$

The E.M.F. of S_2 is very small, as before mentioned, being about 0.025 volt, and that is the reason why in this case the cells were connected in series—i.e., because if S_2 had been put in circuit alone, the ratio of the E.M.F. of S_2 to that of the working cell A would have been such as to cause the balance to come very near the end of the scale, and hence the result would have been very unreliable. Having determined the E.M.F. of S_2 , and knowing the difference of potential for the calomel electrode, the difference of potential for the $\text{Cu} | n\text{CuSO}_4$ can be calculated. Care must be taken in noting the algebraic sign.

For example—

$$\begin{array}{lcl} \text{Cell} & \text{Cu} | n\text{CuSO}_4 & \text{Calomel} \\ 0.025 = & x & + (-560) \\ \therefore x = & 0.585. & \end{array}$$

Experiment: Repeat the Above Experiment, substituting $\text{Zn} | n\text{ZnSO}_4$ Electrode for the $\text{Cu} | n\text{CuSO}_4$ Electrode—In this case the cells S_1 and S_2 should not be connected in series, but put in the circuit independently, as the E.M.F. of the cell $\text{Zn} | n\text{ZnSO}_4 | 3n\text{KCl} | \text{Hg}_2\text{Cl}_2 | \text{Hg}$ is sufficient to give a satisfactory bridge reading alone—

$$\text{Then—} \quad \frac{\text{E.M.F. of Weston}}{\text{E.M.F. of } S_2} = \frac{x_1}{x_2},$$

x_1 being the reading when Weston is in circuit, and x_2 when S_2 is in circuit.

$$\text{E.M.F. of } S_2 = \text{E.M.F. of Weston} \times \frac{x_2}{x_1}.$$

$$\text{E.M.F. of } S_2 = 1.019 \times \frac{x_2}{x_1} \text{ volts.}$$

The result should be about 1.08 volts. From this calculate the electrode potential as before.

In the same way determine the electrode potentials for $\text{Cu} \mid \frac{n}{10}\text{CuSO}_4$ and $\text{Zn} \mid \frac{n}{10}\text{ZnSO}_4$.

If time permits, determine the E.M.F. of several of the following combinations—



In each case check the results by comparing them with the algebraic sum of the electrode potentials determined in the previous experiments.

We have seen that for a single electrode or half-element the difference of potential between the metal and the solution can be represented by the equation—

$$E = \frac{0.058}{n} \log_{10} \frac{P}{p},$$

where P is the solution pressure of the metal, and p the osmotic pressure of the metal ions in solution.

If E_1 is the E.M.F. of one electrode and E_2 the E.M.F. of another electrode, then the E.M.F. of the combination will be—

$$E = E_1 - E_2 = \frac{0.058}{n} \left(\log_{10} \frac{P_1}{p_1} - \log_{10} \frac{P_2}{p_2} \right),$$

where E_1 and E_2 have their correct sign.

Influence of Change of Concentration of Salt Solution on the E.M.F. of a Cell—In the above equation C_1 can be substituted for P_1 where C_1 represents an ionic concentration, which would just balance the solution pressure P_1 , similarly C_2 for P_2 .

For p_1 and p_2 the corresponding ionic concentrations may be substituted.

Hence the equation may be written—

$$E = E_1 - E_2 = \frac{0.058}{n} \left(\log_{10} \frac{C_1}{c_1} - \log_{10} \frac{C_2}{c_2} \right).$$

It is obvious that the influence of dilution on any given electrode will depend upon whether ions are going into the solution from the metal, or being deposited on it from the solution. In the former case dilution would increase the E.M.F. of the electrode; more ions would tend to pass into solution. In the latter case dilution would diminish the E.M.F. of the electrode, as the tendency to deposit ions on the metal would be reduced.

If the metal is the same in both the electrodes—i.e., the only difference between them being the concentration of the salt solution—then the solution pressure will be the same on both sides—i.e., P_1 and P_2 , therefore $C_1 = C_2$, hence the equation simplifies to—

$$E = E_1 - E_2 = \frac{0.058}{n} \left(\log_{10} \frac{c_2}{c_1} \right).$$

If we consider a single half-element, then say—

$$E_1 = E_2 + \frac{0.058}{n} \left(\log_{10} \frac{c_2}{c_1} \right),$$

where E_2 is the *electrode potential* for ionic concentration c_2 , and E_1 for ionic concentration c_1 . If $c_1 = 1$, the equation becomes—

$$E_1 = E_2 + \frac{0.058}{n} \log_{10} c_2.$$

Hence, if the concentration be increased or decreased ten times, the potential difference will change by $\frac{0.058}{n}$ volts.

Let α_1 and α_2 be the degrees of ionization at concentration, x_1 and x_2 of total concentration of salt, then $c_1 = \alpha_1 x_1$ and $c_2 = \alpha_2 x_2$.

Given that α for $n\text{CuSO}_4 = 0.21$, and for $\frac{n}{10} \text{CuSO}_4 = 0.38$, using these values for α , compare the above theory with results obtained in the previous experiment for $\text{Cu} | n\text{CuSO}_4$, and $\text{Cu} | \frac{n}{10} \text{CuSO}_4$, assuming one of them.

Experiment to Determine the Electrode Potential between Silver and Silver Nitrate Solutions, at Concentrations n and $\frac{n}{10}$ —Two silver electrodes are made in a manner similar to that de-

scribed for zinc and copper. In this case the electrode must be coated with a fine deposit of silver by electrolysis, in a manner similar to copper (using AgNO_3 and HNO_3 instead of CuSO_4 and H_2SO_4). The electrodes must be tested as before. Fill one tube with normal silver nitrate solution, and the other with $\frac{n}{10}$ silver nitrate solution. Combine them independently with a calomel electrode by means of an indifferent electrolyte, such as normal potassium nitrate. Then measure the E.M.F. of each cell, as previously described.

Given that α for normal silver nitrate is 0.58, and for $\frac{n}{10}$ 0.81, and using the value for the normal silver nitrate electrode for E_2 in the equation—

$$E_1 = E_2 + \frac{0.058}{n} \log_{10} \frac{c_2}{c_1}.$$

Calculate what the value for E_1 ought to be, and compare it with the experimental result (see next experiment).

Experiment: Determination of E.M.F. of a Cell in which the Two Silver Electrodes differ only in Concentration of Silver Nitrate Solution—Combine the two silver electrodes prepared as previously directed, giving the combination—



Determine the E.M.F. as previously described. It will be observed that silver is deposited from the more concentrated solution, while the silver dissolves in the weaker solution—i.e., the concentrations of the two solutions tend to equalize. When this point is reached, no current passes.

$$\alpha \text{ for } n\text{AgNO}_3 = 0.58; \alpha \text{ for } \frac{n}{10} \text{AgNO}_3 = 0.81.$$

Then—

$$\frac{c_2}{c_1} = \frac{0.58}{0.081} = 7.17; n = 1 \text{ in equation.}$$

$$\therefore E = \frac{0.058}{n} \log_{10} 7.17.$$

$$\therefore E = 0.049 \text{ volt.}$$

The experimental result should be within 2 millivolts of this value.

When we have a cell in which the electrodes only differ in the concentration of the salt solution, the cell is termed a *concentration cell*. Such a cell is the one used in the last experiment.

Up to the present we have assumed that the contact potential of the two liquids has been illuminated, but in cells of this type the contact potential must be considered, since in some cases the contact E.M.F. may be quite an appreciable fraction of the total E.M.F.

It can be shown that the contact difference of potential between two solutions is due to the different velocities of the two ions, and the dilute solution takes the potential, corresponding with that of the more rapid ions.

The contact potential between two solutions of same electrolyte will be—

$$E = \frac{u-v}{u+v} \cdot \frac{0.058}{n} \log_{10} \frac{c_1}{c_2}.$$

Hence, taking all the junctions in order—

$$E = \frac{0.058}{n} \left[\log_{10} \frac{C_1}{c_1} + \frac{u-v}{u+v} \log_{10} \frac{c_1}{c_2} - \log_{10} \frac{C_2}{c_2} \right].$$

Now, since $C_1 = C_2$ —

$$\begin{aligned} E &= \frac{0.058}{n} \left[\frac{u-v}{u+v} \log_{10} \frac{c_1}{c_2} + \frac{u+v}{u+v} \log_{10} \frac{c_2}{c_1} \right] \\ &= \frac{0.058}{n} \left[-\frac{u+v}{u+v} \log_{10} \frac{c_1}{c_2} + \frac{u-v}{u+v} \log_{10} \frac{c_1}{c_2} \right] \\ &= -\frac{0.058}{n} \cdot \frac{2v}{u+v} \cdot \log_{10} \frac{c_1}{c_2}. \end{aligned}$$

$$\therefore E = -\frac{v}{u+v} \cdot \frac{2 \times 0.058}{n} \log_{10} \frac{c_1}{c_2}.$$

$\frac{v}{u+v}$ represents the transport number of the anion, and c_2 and c_1 are the ionic concentrations of the metal ions in the two solutions.

We have already seen (p. 127) that if we know the ionic concentrations of the metal ions in the two electrodes we can calculate E. Hence, if we determine E experimentally, and then, using the above equation, if we know also the transport

number of the anion and the ionic concentrations of one of the solutions, we can calculate the ionic concentration of the other solution.

Experiment to Determine the Concentration of Silver Ions in $\frac{n}{100}$ Solution of Silver Nitrate—Prepare cell $\text{Ag} \mid \frac{n}{10} \text{AgNO}_3 \mid \text{KNO}_3 \mid \frac{n}{100} \text{AgNO}_3 \mid \text{Ag}$, and determine E.M.F. as before.

The transport number for the anion is 0.53, and the degree of ionization for $\frac{n}{10} \text{AgNO}_3$ is 0.81.

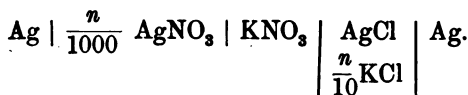
$$\therefore E = 0.53 \times 2 \times 0.058 \log_{10} \frac{0.081}{x}.$$

E is determined experimentally, hence x can be calculated. The degree of ionization for $\frac{n}{100} \text{AgNO}_3$ will be $100x$, x the ionic concentration.

The correct value for x is 0.0093, but the above concentrations do not rigidly obey the gas and dilution laws, hence the experimental value of x is not quite correct. An error up to 10 per cent. is allowable.

Experiment: Determination of the Solubility of Silver Chloride in Water by E.M.F. Measurements—The previous experiment shows that the degree of ionization of a salt can be easily determined from the E.M.F. measurements. In the case of electrode $\text{Ag} \mid \text{AgCl}$ the ionic concentration of the silver chloride solution is very small, hence its conductivity will be low; in such a case another more suitable soluble electrolyte is added, usually with a common ion. In this case $\frac{n}{10} \text{KCl}$ is very suitable, by this means the conductivity is increased and the results rendered more accurate.

Prepare cell—



Electrode $\text{Ag} \mid \text{AgCl} \mid \frac{n}{10} \text{KCl}$ is prepared by first adding the $\frac{n}{10} \text{KCl}$, and then adding two drops of silver nitrate to give

a precipitate of silver chloride, thereby giving as a saturated solution of AgCl in KCl solution.

Determine the E.M.F. as before, then we have—

$$E = 0.53 \times 2 \times 0.058 \log \frac{0.001}{x}$$

—i.e., assuming ionization is complete—i.e., $\alpha = 1$. Hence x , the ionic concentration of Ag in the $\text{AgCl} \frac{n}{10} \text{KCl} | \text{Ag}$, corresponds to the solubility of silver chloride, since silver chloride is completely ionized.

Again, the concentration of the chloride ions and silver ions must be equal—i.e. $= x$.

$$\therefore \text{solubility product} = x^2 = K.$$

Hence $\sqrt{K} = x$ is the solubility of silver chloride in the solution. The value is 1.15×10^{-5} gram equivalents per litre.

Gas Cells—So far we have been concerned with cells in which we had soluble reversible electrodes. Insoluble electrodes, which do not give rise to metallic ions, such as platinum, can be prepared. By coating the platinum with finely divided platinum, it acquires the power of absorbing gases. If such an electrode is immersed in an electrolytic solution, say HCl solution, and say hydrogen bubbled through, a certain amount of hydrogen is absorbed by the platinum, and a difference of potential will be established between the solution and the metal. The electrode in this case behaves like a sheet of metallic hydrogen. If positive electricity passes through the solution, hydrogen ions are discharged $2\text{H}^+ \longrightarrow \text{H}_2$, if negative, the gaseous hydrogen becomes ionized $\text{H}_2 \longrightarrow 2\text{H}^+$.

An electrode of the above type is known as a *hydrogen electrode*. An oxygen electrode behaves similarly.

Preparation of Hydrogen Electrode—The glass portion of the apparatus is very similar to that used for the calomel electrode. A convenient form is as shown in Fig. 66.

It consists essentially of a fairly wide glass tube, *A*, with a tube, suitably bent, sealed into the bottom. This is the inlet tube for the gas. The electrode consists of a piece of platinum foil 2×1.5 cms., to which is welded a piece of

platinum wire, and this in turn is sealed into a glass tube. The electrode is held in position by means of a rubber stopper. Connection with a second electrode is made by means of a side tube, *C*. The gas escapes through side tube *D*, which is provided also with an air trap, *F*.

The electrode must be coated with an even layer of platinum black. This is best done as described on p. 106, the electrode being previously cleaned with hot potassium bichromate and dilute sulphuric acid. For efficiency of the

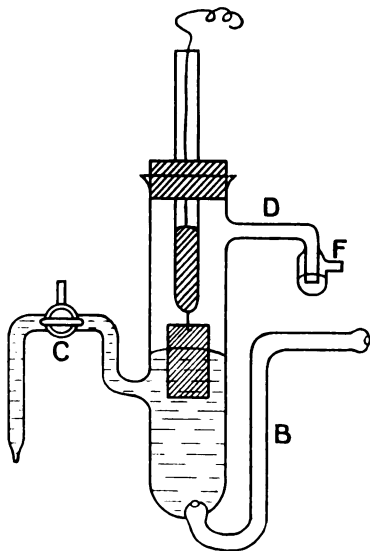


FIG. 66

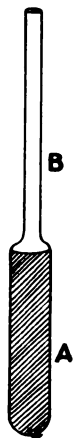


FIG. 67

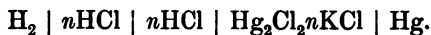
electrodes, the coating of platinum black should be quite uniform and fairly thick, since the amount of gas absorbed will depend upon the thickness of the coating. The occluded impurities, chiefly chlorine, may be removed by immersing the electrode in an acidified (H_2SO_4) solution of a mixture of ferrous and ferric sulphate for about twenty minutes. Then thoroughly wash the electrodes with distilled water. If not required for use immediately, preserve it in distilled water.

Another form of electrode is as indicated in Fig. 67. It

consists of a hard glass tube, *A*, sealed on to a narrow tube; *B*. A short piece of thin platinum wire is sealed into *A* at *C*. The tube is thoroughly cleaned, and then bulb *A* coated with an even layer of "liquid platinum" (see Appendix). The tube is then carefully warmed. Raise the heating slowly as the film dries and darkens, becoming almost black. Then heat the tube to dull redness, taking care not to let the tube soften. The tube should, on cooling, be coated with a fine grey metallic film of platinum. The wire *C* makes a contact with this film, so by means of a little mercury poured into the tube a contact can be made between the film and the rest of the apparatus.

The first form of electrode has the disadvantage that it requires several hours for the gas in the electrode and solution to attain equilibrium, and hence a constant potential. The second type gives a constant potential much quicker, but on the whole is not so efficient and reliable as the type in which rectangular sheets of platinum are used.

Experiment: Determination of Electrode Potential of the Hydrogen and Normal Hydrochloric Acid Electrode—Prepare a normal solution of pure hydrochloric acid, and fill up the electrode to just about the side tube *C*. Fix the platinum electrode so that just over half of it is immersed. The trap *F* should contain a little mercury. Open tap *C* (which need not be lubricated with vaseline) and pass in a slow current of hydrogen, which has been made to pass through potassium permanganate solution, and then through silver nitrate solution, and finally through normal hydrochloric acid solution, before entering the electrode. Close exit *F*, thereby forcing some of the acid through *C*, filling the tube; then close tap *C*, at the same time opening *F*. Now allow the hydrogen to bubble through for at least an hour (longer if possible) to completely saturate the electrode with hydrogen. Now complete the cell—



—i.e., join up with a calomel electrode by means of normal hydrochloric acid. The tap *C* should be kept closed, since if the barrel is wetted with the solution it will be a sufficiently good conductor. The hydrogen should bubble through only very slowly. Now determine the E.M.F. of the cell by balancing it against a Weston cell, exactly as in previous

experiments. In this case it is necessary to determine the E.M.F., say, every fifteen minutes, until the consecutive readings practically coincide.

Then, knowing the E.M.F. of the cell and the electrode potential for the calomel electrode, the electrode potential for electrode can be calculated as in previous experiments.

An electrode such as the above, in which the hydrogen is at atmospheric pressure, and normal acid used, is sometimes taken as the standard of potential difference.

The E.M.F. is 0.277 volt.

Experiment to Determine E.M.F. of a Hydrogen Concentration Cell—Prepare cell—



Take the same precautions with each electrode as described in previous experiment for the hydrogen electrode. Determine the E.M.F. every fifteen minutes, until the E.M.F. is constant.

The E.M.F. in this case is small, so put the cell in *series* with the Weston cell. Having determined the E.M.F. of the cell, determine the degree of ionization of hydrochloric acid in normal solution, given that $\frac{v}{u+v} = 0.17$ and the degree of

ionization for $\frac{n}{10}$ hydrochloric acid is 0.91.

$$E = 0.17 \times 2 \times 0.058 \log_{10} \frac{a_1 c_1}{0.091} [c_1 = 1].$$

Extension—In a similar manner the student might determine the E.M.F. of—



—i.e., hydrogen-chlorine cell.

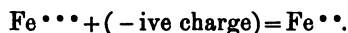
Electrical Potentials of Oxidation and Reduction Media—When an indifferent electrode, such as platinum or iridium, is placed in an oxidizing solution, it will acquire a positive charge relative to the solution; and if placed in a reducing solution, it will acquire a negative charge.

If a change from a higher to a lower state of oxidation occurs, then a positive charge is given up or negative charge

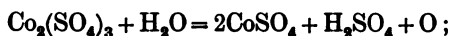
taken up. Hence change of ferric ion to ferrous ion may be represented thus—



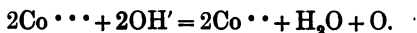
or



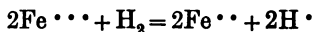
Reducing agents act in the reverse way. When an oxidizing salt is present in aqueous solution, its affinity for a negative charge will tend to take such a charge from the hydroxyl ions, thereby liberating oxygen. For example, if cobaltic sulphate is dissolved in water and sulphuric acid added, the affinity is sufficient to cause the liberation of oxygen.



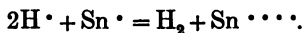
or



Consider a cell made up of a hydrogen electrode on one side and a platinized electrode dipping in a solution of a ferrous and ferric salt on the other, connected up with some indifferent electrolyte. When these electrodes are joined together, the current goes from the hydrogen electrode to the other *in the cell*. Hence the hydrogen is going into solution—*i.e.*, acquiring a positive charge—hence at the other electrode the ion is losing corresponding charge. The total change will be—



—*i.e.*, the ion is reduced. When the cell is reversed, $\text{Fe}^{\bullet\bullet}$ will be converted in $\text{Fe}^{\bullet\bullet\bullet}$; and hydrogen will be liberated. If, on the other hand, the platinum electrode dips into a solution of stannous chloride in potassium hydroxide, and connected with a hydrogen electrode so as to form a cell, the current passes from the solution to the hydrogen electrode *in the cell*—*i.e.*, hydrogen ions are discharged, and the stannous ion acquires two positive charges, becoming stannic.



In the first case the solution is said to have an *oxidation potential*, and in the second case a *reduction potential*.

Measurement of Oxidation Potentials: Experimental Determination of Electrode Potential of Ferric-Ferrous Salt Electrode—Both oxidation and reduction potentials are measured in a precise

similar manner as that used for the measurement of single potential differences between metals and salt solutions.

Prepare a solution containing 0.09 gram molecule FeCl_3 + 0.01 gram molecule FeCl_2 per litre. Prepare also a platinized platinum electrode as directed for hydrogen electrode. Fit up an electrode similar to the metal salt solution electrode previously described—*i.e.*, platinum electrode immersed in the iron salt solution. Complete the cell by combining it with a normal hydrogen electrode $\text{H}_2 \mid n\text{KCl}$ by means of an electrolyte such as normal KCl. The E.M.F. of this cell is then determined in exactly the same manner as in previous experiments (see Fig. 62). Then, taking the hydrogen electrode potential as 0.277 volt, the oxidation potential can be determined.

The result should be about 0.43 volt.

Further experiments may be done in a similar manner with the following oxidation media :

0.01 Mol FeCl_3	0.09 Mol FeCl_2	...	0.32 volt.
0.1 normal HMnO_4	...	...	1.18 volts
HNO_3 , 6 per cent.	...	...	0.67 volt
HNO_3 , 35 per cent.	...	...	0.75 "
HNO_3 , 90 per cent.	...	...	0.82 "

Measurement of Reduction Potentials—These measurements are carried out in precisely the same manner as in the above experiments.

Experiments—Measure the reduction potentials with the following media :

Normal Cu_2Cl_2 in concentrated HCl ;

$\frac{n}{10}$ SnCl_2 in $5n\text{HCl}$.

CHAPTER XVI

VELOCITY OF CHEMICAL REACTION

ALL chemical reactions require time for their accomplishment. The actual velocity of the reaction is governed mainly by Guldberg and Waage's law of mass action, according to which the velocity of reaction at any moment is proportional to the concentrations of the substances taking part in the reaction. Consider a simple reversible reaction, such as ester formation, in which a, b, c, d are the initial equivalent concentrations of the reacting substances. Let x be the amount of ester formed in the time t , the equation for the velocity of reaction at any instant will be—

$$\frac{dx}{dt} = K(a-x)(b-x) - K_1(c+x)(d+x),$$

where dx is the increase in the amount of x during the small interval of time, dt . In many cases it will happen that the reaction is reversible only to a very slight extent, and K_1 becomes negligible in comparison with K . When such is the case, the equation simplifies down to—

$$\frac{dx}{dt} = K(a-x)(b-x).$$

The simplest type of chemical reaction is that in which only one substance is undergoing change, and there is practically no back reaction. A reaction in which only one molecule of a single substance is undergoing change is termed *unimolecular reaction*, or a *reaction of the first order*.

Unimolecular Reactions—In cases where the reaction is unimolecular, the equation becomes—

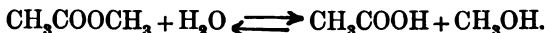
$$\frac{dx}{dt} = K(a-x),$$

which on integration gives—

$$K = \frac{1}{t} \log_e \frac{a}{a-x};$$

$$= 2.302 \left[\frac{\log_{10} a - \log_{10} (a-x)}{t} \right].$$

Hydrolysis of Methyl Acetate in Presence of Hydrochloric Acid—When methyl acetate is acted upon by water, it is partially converted into methyl alcohol and acetic acid. When the amount of water is relatively large, the *hydrolysis* is practically complete—that is to say, the following equation goes from left to right—



The rate of hydrolysis is greatly accelerated by the presence of acids, and is, in fact, proportional to the concentration of the hydrogen ion.

Experiment—Prepare a standard solution baryta, approximately $\frac{n}{20}$, and determine its actual value by titration against pure succinic acid, using phenolphthalein as an indicator. Make up also a semi-normal solution of hydrochloric acid, standardizing it by means of baryta solution (the water used should be free from CO_2). Clean two small Erlenmeyer flasks with steam, and dry them. Fit them with corks which have been previously soaked in paraffin. It is also necessary to weight the flasks with a ring of lead, in order to make them sink to a convenient depth in the water of the thermostat. Two other Erlenmeyer flasks, about 100 c.c. capacity, fitted with corks, will be required in which to carry out the titrations; also three pipettes, one delivering 20 c.c. and two delivering 2 c.c., also a small stoppered bottle containing pure methyl acetate. Into one of the small Erlenmeyer flasks introduce 20 c.c. of $\frac{n}{2}$ HCl, and into the other 40 c.c. of $\frac{n}{2}$ HCl. Suspend the flasks in a thermostat at 25° , so that they are immersed up to the neck, also suspend the bottle containing the methyl acetate in the thermostat.

When the liquids have assumed the temperature of the bath (*i.e.*, about fifteen minutes), introduce 2 c.c. of methyl

acetate into one of the flasks of acid, shake well, and at once remove 2 c.c. of the mixture. This is run into about 50 c.c. of ice-cold water, free from CO_2 , in order to arrest the reaction, it is then titrated as quickly as possible with baryta solution. The moment when the mixture was diluted must be noted. In this way the initial concentration of the acid is determined. Now introduce 2 c.c. of methyl acetate into the other flask of acid, and find the concentration of the acid in this case exactly as before, taking care to note the time when the reaction is arrested.

About ten minutes after the first titration, again withdraw 2 c.c. of the mixture from each of the flasks, and determine, as before, the concentration of the acid, noting carefully in each case the moment when the reaction is arrested. Go through the same procedure after intervals of 20, 30, 40, 60, 120 minutes from the starting-point, and then, after forty-eight hours, carry out the final titration. Now, if the initial titration is T_0 , and the final titration T_∞ , then a is proportional to $T_\infty - T_0$, and $a - x$ is proportional to $T_\infty - T_n$, where T_n is the titration after n minutes; hence we get—

$$K = 2.302 \left[\frac{\log_{10}(T_\infty - T_0) - \log_{10}(T_\infty - T_n)}{t_n} \right].$$

Thus to calculate K it is not necessary to calculate the actual amount of ester hydrolyzed, but the value of K can be obtained directly from the titration readings.

The velocity constant can be calculated from any stage in the reaction. For example, if T_x and T_y are the titrations at the times t_x and t_y , then we have—

$$K = 2.302 \left[\frac{\log_{10}(T_\infty - T_x) - (T_\infty - T_y)}{t_y - t_x} \right].$$

The above experiment should now be repeated, using semi-normal H_2SO_4 .

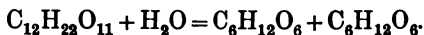
Assuming that the velocity constants are directly proportional to the degree of ionization of the respective acids, calculate the degree of ionization of H_2SO_4 in semi-normal solution given—

$$\alpha \text{ for } \frac{n}{2} \text{ HCl} = 0.85.$$

The value of α for $\frac{n}{2} \text{ H}_2\text{SO}_4$ is 0.53.

Exercise—Plot the values of x against the corresponding values of time, and draw a smooth curve.

Velocity of Inversion of Cane Sugar—Another very interesting reaction of the first order is the hydrolysis of cane sugar into dextrose and lævulose. This is represented by the equation—



As the acid which accelerates the hydrolysis *remains unaltered* at the end of the reaction, it does not occur in the equation. The reaction can be conveniently followed by measuring the change in the rotation of the plane of polarized light. Whereas cane sugar is dextro-rotary, invert sugar is lævo-rotary, so that the result of inversion is that the sign of rotation changes from right to left.

As both sugar and water take part in the reaction, the velocity equation, according to the law of mass action, is—

$$\frac{dx}{dt} = K.C_{\text{Sugar}}.C_{\text{Water}}.$$

Since, however, the water is present in great excess, its concentration, and therefore its active mass, remain practically constant throughout the reaction, and the equation therefore reduces to one of the first order.

The amount of cane sugar present at any time is proportional to the difference between the angle of rotation at that time and the angle of rotation at the end of the reaction.

If A_0 represents the initial angle, and A_∞ the final angle of rotation after complete inversion has occurred, and A_n the angle of rotation after time t_n , then the initial amount of cane sugar will be proportional to $A_0 - A_\infty$ —i.e., total change in rotation—and $A_n - A_\infty$ the amount of cane sugar present after time t_n —i.e.—

$$a = A_0 - A_\infty \text{ and } (a - x) = A_n - A_\infty.$$

$$\therefore K = 2.302 \left[\frac{\log_{10}(A_0 - A_\infty) - \log_{10}(A_n - A_\infty)}{t_n} \right].$$

If K is calculated for any two readings, say t_x t_y , the equation becomes—

$$K = 2.302 \left[\frac{\log_{10}(A_x - A_\infty) - \log_{10}(A_y - A_\infty)}{t_y - t_x} \right].$$

The values of the angles must be given their correct sign, rotations to the right being +, and those to the left -.

Experiment—Prepare a solution of cane sugar by dissolving 20 grams of pure cane sugar in water, and making the volume up to 100 c.c. If the solution is not clear, filter and add a crystal of camphor as a preservative. Prepare also a normal solution of hydrochloric acid.

Place 30 c.c. of the sugar solution and 30 c.c. of HCl solution in separate flasks, which have been thoroughly cleaned and dried, and suspend the flasks in a thermostat at 25° C. Set up a polarimeter, and place a clean, jacketed, observation tube in the polarimeter. Circulate water at 25° C. between the jacket and the observation tube (see Fig. 36), and determine the zero (see Polarimeter Measurements).

Mix the acid and sugar solutions thoroughly, and, as soon as possible, fill the observation tube with the mixture, and determine the angle of rotation. Note the time at which the reading is made.

The angle of rotation changes rather rapidly at first, so take five or six readings in succession, and note the time for the first and last of these readings. The mean value of the angles should be taken as A_0 at the time, halfway between the first and last reading being taken as the starting-point of the reaction. Take subsequent readings after 10, 20, 40, 60, 120 minutes, and a final reading after forty-eight hours, the tube being kept during this latter period in a thermostat. Calculate the value of K from the equation given.

The value for a 20 per cent. sugar solution, with equal volume of normal HCl at 25°, is 0.00472.

The experiment should be repeated with normal H_2SO_4 .

Note—The value of zero should be redetermined at the end of the experiment, in order to see that it has been constant during the experiment.

Bimolecular Reactions—When two substances react and both alter in concentration, the reaction is said to be *bimolecular or of the second order*. If the initial molecular concentration of one substance is a , that of the other b , and x the amount transformed in the time t , the velocity equation is—

$$\frac{dx}{dt} = K(a - x)(b - x).$$

When the substances are present in equivalent quantities, the equation becomes—

$$\frac{dx}{dt} = K(a-x)^2,$$

which on integration gives—

$$K = \frac{1}{t} \frac{x}{a(a-x)}.$$

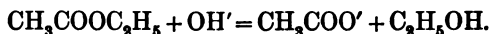
When the reacting substances are not present in equivalent proportions, the calculation is somewhat more complicated on integrating—

$$\frac{dx}{dt} = K(a-x)(b-x)$$

we get—

$$\begin{aligned} K &= \frac{1}{(a-b)t} \cdot \log_e \frac{(a-x)b}{(b-x)a} \\ &= \frac{2.302}{(a-b)t} \log_{10} \frac{(a-x)b}{(b-x)a}. \end{aligned}$$

Experiment: Saponification of Ethyl Acetate with Sodium Hydroxide—In this case the velocity of saponification is approximately proportional to the concentration of OH' ions—



This reaction differs from the hydrolysis by acids, where the concentration of H ion remains unchanged; in this case the concentration of the OH' ion changes throughout the experiment.

Make up $\frac{n}{60}$ solution of ethyl acetate. Place 50 c.c. in an Erlenmeyer flask (100 c.c.), fitted with a paraffin cork, and suspend in a thermostat at 25°. Into a similar flask introduce 50 c.c. of $\frac{N}{40}$ NaOH (free from carbonate), and suspend this also in the thermostat. When these two solutions have acquired the temperature of the thermostat, pour the alkali into the ester, and shake the mixture well. The initial alkali concentration is calculated from the amount of alkali added, after correcting for the amount of alkali which has remained on the sides of the flask; the latter is found by titration.

After intervals of 3, 5, 10, 20, 30, 60, 90 minutes, 5 c.c. of the mixture is withdrawn and run into a known volume of $\frac{n}{20}$ HCl. The excess of acid is found by titration with baryta.

The mean point of the time taken to introduce the 5 c.c. mixture into the acid is taken as time at which the reaction was stopped. The final titration should be taken after twenty-four hours.

K can then be calculated from the following equation—

$$K = \frac{2.302}{T_{\infty}t} [\log_{10} T_t + \log_{10}(T_0 - T_{\infty}) - \log_{10} T_0 - \log_{10}(T_t - T_{\infty})],$$

where T_0 , T_t , T_{∞} are the numbers of cubic centimetres of acid required to neutralize the amount of alkali in the mixture at the beginning of the reaction, after the interval of time, t , and at the end of the reaction respectively. The actual value of K obtained depends on the normality of the solutions when it is calculated in the manner indicated above, but the value which would be obtained with normal solutions can be calculated by multiplying the above expression by $\frac{V}{N}$, where V is the number of cubic centimetres removed for each titration, and N the normality of the standard acid; in this case 5 and $\frac{1}{20}$ respectively.

Determination of the Order of a Reaction—Velocity measurements are made with definite concentrations of the reacting substances, and with double and treble those concentrations, determining in each case the times taken to complete a definite fraction (say one-third) of the total change. Then, according to Ostwald, the order of reaction can be determined as follows:

1. For a reaction of the first order, the time taken to complete a certain fraction of the reaction is independent of the initial concentration.

2. For a reaction of the second order, the time taken to complete a definite fraction of the reaction is inversely proportional to the initial concentration—i.e., if the concentration is doubled, the time is halved to complete the same fraction of the reaction.

3. Generally speaking, for a reaction of the n th order, the times taken to complete a certain fraction of the reaction are inversely proportional to the $(n-1)$ power of the initial concentration.

CHAPTER XVII

QUANTITATIVE ELECTROLYTIC ESTIMATIONS

Quantitative Electrochemical Analysis. Electrolytic Determination of Metals—There are many advantages in favour of electrolytic methods, where available, over the usual gravimetric method. The latter are frequently very laborious, and at the same time the chances of error are not by any means small. The electrolytic methods, on the other hand, are usually very much simpler, quicker, and determination can be made with a very high degree of accuracy, hence electrolytic methods are coming more and more into use, particularly in the commercial world. The metals are usually estimated in the form of the pure metal or in the form of a metallic oxide. In order to make a successful determination it is essential that the metal should be obtained as a very fine deposit firmly adhered to the cathode, and as smooth as possible, so that it can be well washed without any marked loss. If, on the other hand, the deposit is coarse or granular, it is very liable to be lost in the washing of the deposit, and at the same time is liable to be impure. In order to obtain a successful deposit *the potential difference, temperature, and current density* must be carefully controlled.

Apparatus—The most suitable form of apparatus is as shown in Fig. 68. A light platinum dish, *A*, serves as the cathode, and is supported on a suitable stand by means of a metal ring. The anode *B* is usually of the form of a flat spiral of platinum, or in some cases a flat perforated platinum plate welded to a platinum wire, the object of the perforations being to allow the escape of gas which would otherwise collect under the plate. The other connections are as shown in Fig. 67. The current and voltage are noted by means of an ammeter, *M*, and voltmeter, *V*, respectively, the voltmeter being placed between

the anode and cathode. Another simpler form of apparatus is as shown in Fig. 69, the hollow platinum cylinder being used instead of a platinum dish, and the apparatus being placed in a beaker.

In all experiments it is necessary to know the *current density* at the electrodes. In the case of metallic depositions the current density at the cathode only is required. The current density is usually expressed in ampères per square centimetres, or ampères per 100 square cms. Hence the surface of the electrode used must be calculated. This may be done once for all for a given volume of liquid in the basin.

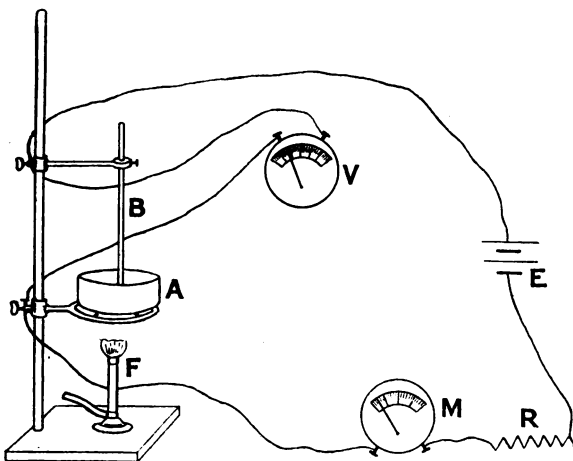


FIG. 68

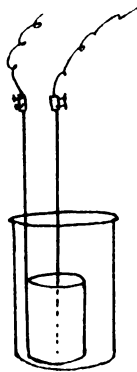


FIG. 69

Experiment : Electrolytic Determination of Copper—Weigh out accurately 1 gram of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and dissolve in a little water (distilled); transfer to the platinum basin, adding the washings, and make up to a suitable volume, then add 3 per cent. by volume of nitric acid. Heat the solution to about 50° to 60°C. , and keep the temperature approximately constant by placing a small flame under the basin. Pass a current of E.M.F. 2.2 to 2.5 volts and a current density 0.5 to 2.5 ampères per 100 square cms. The nitric acid becomes gradually weaker during electrolysis, so from time to time a few more drops should be added. The dish should be covered with a

clock-glass, which has a hole in the centre for the anode wire to pass through. To test whether the copper has been completely deposited, add a few cubic centimetres of distilled water, thereby raising the level of the liquid in the basin, and note whether any copper is deposited on the fresh surface.

The solution is tested finally by removing a drop of the liquid by means of a glass rod, and touching a drop of ammonia solution on a white tile. If the deposition is incomplete, a blue colour will result.

When the whole of the copper has been deposited it is essential to remove the liquid before the current is stopped, otherwise the nitric acid will redissolve some of the copper. First dilute the solution with distilled water, then syphon off the liquid by first filling a bent glass tube with water, closing one end with the finger, and then putting the other end of the tube below the surface of the liquid in the basin, then, on removing the finger, the liquid will siphon over. As the liquid is removed from the basin the distilled water must be added so as to keep the electrodes wholly immersed. This is done until the acid is too dilute to affect the copper. The current is stopped, the basin removed, and the deposit washed once or twice with distilled water and then with alcohol, and finally dried in an air oven at 80° . The basin + deposit is then weighed, and then, by subtracting the weight of the basin, the amount of copper can be estimated. *Note*—the deposit should be perfectly smooth and uniform.

Technical Application of the Above Method—A solution containing copper and metals of the iron group can be analyzed quantitatively for copper by the above method, since the iron group metals remain dissolved in the nitric acid. Commercial copper and many copper ores frequently contain as impurity arsenic and antimony; on electrolysis some of the arsenic and antimony are deposited also, giving a brownish colour to the copper. In this case the deposit is dried and weighed as before, and then ignited over a bunsen flame. The arsenic and antimony volatilize, leaving the copper as copper oxide. This is dissolved in dilute nitric acid, and the copper once more deposited, washed, dried, and weighed as before. The difference in the last two weighings gives the amount of arsenic and antimony which had been deposited.

The above method is frequently used to estimate copper, in simple commercial alloys such as copper-aluminium, etc.

Electrolytic Estimation of Lead—In this case the lead is not estimated as metallic lead, but in the form of peroxide. The deposit is formed at the anode, so in this experiment the basin is made the anode. If possible, a basin with an unpolished surface is preferable, as the deposit is not as fine as in the case of copper, and the rough surface assists the adherence of the deposit.

Experiment—Weigh out into the basin about 1 gram of, say, lead nitrate, dissolve in distilled water, add nitric acid until the solution contains 10 per cent. of free nitric acid. Keep the liquid at a temperature of about 55°, and electrolyze with a current of E.M.F. 2·3 to 2·7 volts and current density of 1 to 2 ampères per 100 sq. cms. Test the end-point first by raising the level of the liquid in the basin, and finally by removing a drop on a watch-glass and adding ammonia and ammonium sulphide. Siphon off the liquid as before.

Then carefully wash the hydrated oxide deposit with distilled water, and dry at 185° in an air oven until the weight is constant. From the weight of peroxide calculate the amount of lead. The estimation usually requires one and a half hours. To clean the anode add hot dilute nitric acid and a few crystals of oxalic acid.

Electrolytic Estimation of Nickel—In this case the basin will be the cathode. Dissolve 1·5 grams of nickel ammonium sulphate and 4 grams of ammonium oxalate in water (120 c.c.). Electrolyze with a current density of 1 ampère per 100 sq. cms. and E.M.F. 2·5 to 3·5 volts. Other details as for copper.

Theoretical Explanation of Electrolytic Depositions—We have already seen that the potential between a metal and its salt is given by the equation—

$$E = \frac{0.058}{n} \log_{10} \frac{P}{p},$$

where P is the solution pressure of the metal, and p is the osmotic pressure of the metallic ions in the solution. Now, the potential difference between a metal and its ions may be considered as a sort of affinity of the metal for a certain charge either positive or negative, hence to convert metallic ions into free metal we have only to apply a contrary E.M.F. slightly higher than the potential difference. In this case it is termed the *decomposition potential*, and its value is given by the equation—

$$E = \frac{0.058}{n} \log_{10} \frac{P}{p}.$$

The value of E will, however, be slowly changed as the metal is deposited, since the value of p is changing; but even if the concentration be diminished 10000 times, the change in the decomposition is only $4 \times 0.058 = 0.232$ volt for a monovalent element, and half this for a divalent element, which is comparatively small.

Suppose, then, we have a solution of two metals whose decomposition potentials are not too near the same value, then it is possible to separate the metals by carefully adjusting the potential difference applied to the solution.

Example Experiment: Determination of Silver and Copper in an Alloy of the Two Metals—Dissolve 0.5 gram of the alloy, 2 c.c. of nitric acid (1 : 3) diluted with water; make up to 150 c.c. Add 5 c.c. of absolute alcohol, and raise the temperature to 55° C. The alcohol and the temperature prevent the formation of silver peroxide at the anode.

Electrolyze the solution with a current of E.M.F. 1.36 ± 0.1 volt and current density 0.5 to 1.5 amperes per 100 sq. cms. Great care must be taken to keep the voltage constant.

When the electrolysis is complete, quickly decant off the solution into a beaker, wash the silver with a little water, add washings to solution, wash with alcohol, and dry at 80° , and weigh. Clean the basin and completely transfer the solution into it, and determine the copper under the conditions for copper—i.e., increase the potential to 2.2 to 2.5 volts.

Quantitative Estimation of Nitric Acid (or Nitrates) by Electrolytic Reduction to Ammonia—Nitric acid or nitrates in the presence of sulphuric acid is reduced at the cathode during electrolysis. The product of reduction depends on the nature of the metal at the electrode. If platinum is used, no ammonia is evolved; but if a little copper salt is added, copper is deposited on the cathode, reduction at once commences, and the greater portion of the nitrate is transformed in ammonium salt.

The ionic equation is—



Under ordinary conditions a certain amount of hydroxylamine is always formed.



The relative proportions of ammonia and hydroxylamine

depend on the physical nature of the electrode. For example, according to Tafel, if a smooth copper electrode is used, 11.5 parts of hydroxylamine to 76.8 parts of ammonia are formed, whereas if the electrode is coated with electro-deposited copper, 1 part of hydroxylamine to 92.3 parts of ammonia results.

The problem is to reduce the production of hydroxylamine to a negligible amount. A small amount of hydroxylamine is counter-balanced by solution of a small amount of copper from the electrode in the sulphuric acid.

Ulsch has succeeded in obtaining conditions under which nitrates can be estimated to within 0.1 per cent.

Apparatus—Prepare a copper cathode. By winding about 2 metres of copper wire 1.4 mm. diameter round a glass tube, 15 mm. diameter, so as to give about forty rounds, are formed. About 15 cms. of wire are left over and bent so as to lie along the axis of the spiral cylinder. Remove the glass tube and draw out the spiral so that each turn is just separated from the next, the total length of the spiral being about 70 mm.

Make an anode of thin platinum wire, supporting it on a glass tube; this passes down the centre of the copper spiral (see Fig. 70). The liquid to be electrolyzed is contained in a test-tube-like tube, 2 cms. diameter, cms. long, the two electrodes being held in position by means of a cork, which must be fitted with an outlet for the gases evolved during electrolysis.

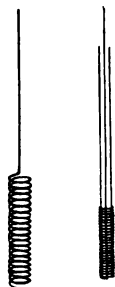


FIG. 70

Prepare the copper electrode by coating it with spongy copper in a copper voltameter (see p. 122), using current density of about 3 ampères per 100 sq. cms.

Experiment: Determine the Amount of Nitrate in a Sample of Potassium Nitrate—Dissolve 0.5 of a gram of potassium nitrate in a little water, and add *exactly* 50 c.c. of normal sulphuric acid. Make up to 100 c.c. with water. Take 20 c.c. of this solution and transfer it to the glass cell and fit the electrodes in position (they should go right to the bottom). If the spiral is not covered, add a little water. Now electrolyze the solution, using an E.M.F. of 4 volts and a current density of 2.5 to 3 ampères per 100 sq. cms. The current density should not be above this, otherwise the amount of hydroxylamine

becomes appreciable. No gas will be evolved at first, since reduction is taking place; but when the reduction is nearing completion, hydrogen is evolved quite freely. When this occurs, continue the electrolysis for a further period of fifteen minutes, to be sure of complete reduction. Remove the electrode carefully before breaking the current; wash then with distilled water, and keep the washing in a beaker. Then transfer the contents of the tube to the beaker containing the washings, and wash out the tube. Then titrate the unused acid with standard alkali.

The equation for the reaction is—



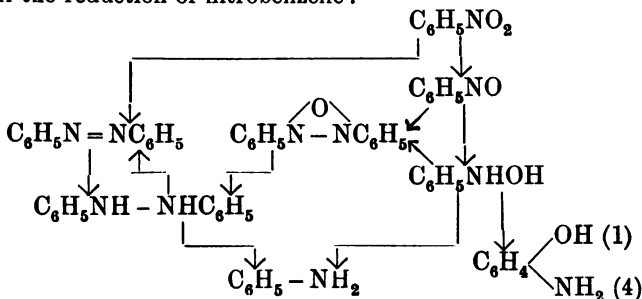
—i.e., two *equivalents* of acid for one equivalent of nitrate. From the amount of acid used (in this case 50 c.c. normal acid) the amount of nitrate can be calculated. With careful manipulation not more than 0.1 to 0.2 per cent. error should be allowed.

CHAPTER XVIII

ELECTROLYTIC PREPARATIONS

Reduction of Aromatic Nitro-Compounds—The final product in the reduction of aromatic nitro-compounds is the amine, but it is possible to obtain a large number of intermediate products, corresponding to the various stages of reduction, by carefully controlling the conditions of the reaction. The whole process is usually a combination of electrochemical reductions and purely chemical reactions. As an example we will consider nitrobenzene.

The following diagram represents all the important changes in the reduction of nitrobenzene :

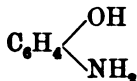


Reduction in Moderately Acid Solutions—The following series of products are formed in which the last is the principal final product :

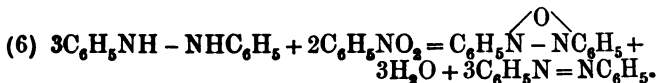
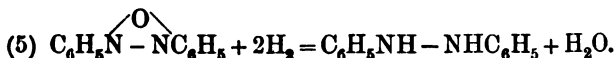
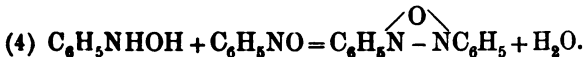
- (1) $\text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{C}_6\text{H}_5\text{NO}.$
- (2) $\text{C}_6\text{H}_5\text{NO} + \text{H}_2 = \text{C}_6\text{H}_5\text{NHOH}.$
- (3) $\text{C}_6\text{H}_5\text{NHOH} + \text{H}_2 = \text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O}.$

Reductions in Strongly Acid Solutions—In this case the reduction stops at the end of equation (2) above—i.e., the principal reduction product being $\text{C}_6\text{H}_5\text{NHOH}.$

Under the influence of the strong acid the phenyl-hydroxylamine is converted into the isomeric para-amido phenol—



Reduction in Alkaline Solution—In this case the equations (1) and (2) are fulfilled, and these combine as follows:



Hence azo-benzene is the principal final product. The reduction of hydrazo-benzene to aniline only takes place to a slight extent.

Preparation of Aniline from Nitrobenzene — Take a tall beaker and place inside a porous pot to serve as the anode chamber, the cathode chamber being the space between the porous pot and the walls of the beaker. The anode consists of strips of sheet lead (about 2 to 3 mm. thick), the cathode is also of sheet lead, but it should be perforated. The cathode is bent in the form of a cylinder so as to encircle the porous pot. Introduce into the anode chamber dilute sulphuric acid of specific gravity 1.1. For the cathode liquor make a mixture of 20 grams of nitrobenzene, 150 c.c. of alcohol, and 125 c.c. of dilute sulphuric acid, specific gravity 1.2. Electrolyze the solution with a current of density 4 to 8 ampères per 100 sq. cms. at the cathode, and voltage about 5 volts. After the passage of about 26 ampère hours, remove a little of the cathode liquid and titrate with sodium nitrite. If the result indicates about 85 to 89 per cent. of the theoretical quantity of aniline, remove the cathode liquid, distil off the alcohol, cool, and about 20 grams of aniline sulphate should crystallize out. The crystals may be decomposed with caustic soda, and the mixture steam distilled.

The o.m.p. toluidines can be similarly prepared, but in the

case of the reduction of *p*-nitrotoluene the percentage is lower.

Preparation of Azobenzene from Nitrobenzene—In this case nickel electrodes are used, otherwise the apparatus is as before. The anode liquid is a cold saturated solution of sodium carbonate, and is contained in the porous cell. The cathode liquid consists of 20 grams of nitrobenzene, 5 grams of crystallized sodium acetate dissolved in 200 c.c. of 70 per cent. alcohol. The cathode density should be 6 to 9 ampères. The electrolysis is carried out at boiling-point, and almost immediately after the theoretical amount of current has been passed (17.5 ampère hours), a considerable amount of hydrogen begins to come off; at this point lower the current density and pass 1 to 2 ampère hours' more current. The contents of the cathode are now free from nitrobenzene, but contains a small amount of hydrazobenzene and azoxybenzene. The bulk of the azobenzene crystallize out almost chemically pure, and may be filtered off on a Buchner funnel. The remainder is precipitated by the addition of water or distilled off in steam, and purified by re-crystallization from alcohol or ether. The current efficiency is over 80 per cent., and the yield is over 90 per cent. of the theoretical amount.

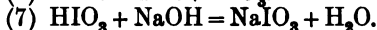
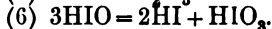
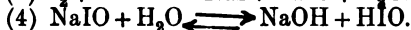
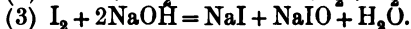
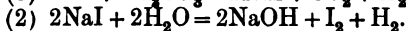
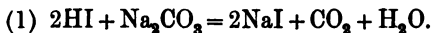
Preparation of Iodoform—When free iodine is warmed with water and an aqueous alkaline solution of alcohol, iodoform is formed according to the following equation:



The hydriodic acid then reacts with the alkali to form iodide. Iodoform is prepared electrolytically by electrolyzing a solution containing potassium iodide, sodium carbonate, and ethyl alcohol. Free iodine is liberated at the anode, which reacts with the alcohol yielding iodoform. The purely chemical method only gives a yield of about 40 per cent., whereas the electrolytic method gives as much as 98 per cent. yield. The anode consists of a large sheet of platinum (or wire gauze), the cathode, which is relatively small, is made of nickel or platinum foil wrapped in parchment. The anode liquid consists of a solution of 20 grams of anhydrous sodium carbonate, 20 grams of potassium iodide, 200 c.c. of water, and 50 c.c. of alcohol (96 per cent.). This solution is poured into the porous cell; the cathode liquor is a solution of sodium carbonate. The

experiment is carried out at 50° to 70°, with a current density at the anode of 1 to 3 ampères per 100 sq. cms., and a cathode current density of 4 to 8 ampères per 100 sq. cms. During electrolysis the solution tends to become alkaline, so a slow stream of carbon dioxide must be bubbled through the cathode liquid so as to neutralize the caustic soda formed. The solution should be from light to dark yellow ; if it becomes brown, interrupt the current of carbon dioxide for a short time.

The electrolysis should be allowed to continue for about three hours in order to get a fair quantity of iodoform. Then on cooling the iodoform separates out, and is filtered off, washed with water, and dried at room temperature. The filtrate, after the addition of fresh quantities of potassium iodide and alcohol, may be used over again, until it contains large quantities of potassium iodate and carbonate. The current efficiency is 80 per cent. The equation given above represents the formation of iodoform, neglecting the intermediate products and secondary reactions. The hydriodic acid reacts with the sodium carbonate to give sodium iodide and carbonic acid. The sodium iodide is continually decomposed by the current, thereby making fresh quantities of iodine available at the anode. The iodine produced at the anode, coming in contact with free alkali or alkali carbonate from the cathode, forms hypiodite, both as alkali salt and as free acid ; this reacts with the alcohol by simultaneous oxidation and iodizing, to produce iodoform and carbonic acid. The chief by-product is alkali iodate, which is produced from that portion of the iodide which does not immediately react with the alcohol.



It is not possible to prepare the corresponding bromoform and chloroform by a similar method, as aldehydes and other products of oxydation of alcohol are given on electrolysis. This is due to the fact that the decomposition potential of

iodine from potassium iodide and soda solution is only 1.12 (normal hydrogen electrode as zero), whilst oxygen is liberated at 1.7. With potassium bromide alcohol and sodium carbonate, bromide separates at 1.75 volts; with potassium chloride chlorine at 2.1 volts.

Preparation of Ammonium Persulphate from Ammonium Sulphate—A porous pot of capacity 100 to 150 c.c. serves as the anode chamber. This is surrounded by a lead spiral, through which cold water can be circulated. A piece of copper connecting wire is soldered on to the lead spiral which forms the cathode. The anode is platinum wire spiral, having a surface of 1 to 2 sq. cms. Fill the anode chamber with a cold saturated solution of ammonium sulphate, the space between the porous pot and the containing beaker—*i.e.*, cathode chamber—being filled with a mixture of 1 part concentrated sulphuric acid and 1 part of water, by volume. The temperature of the anode chamber should be kept between 10° and 20° by circulating iced water through the lead cathode spiral. The anode liquid is kept saturated with ammonium sulphate by suspending in the anode chamber a test-tube, with one or more holes at the bottom, containing solid ammonium sulphate. Pass a current having density of 500 to 1000 ampères per 100 square centimetres at the anode, and a current density as low as possible at the cathode, thereby saving the voltage, and excessive evolution of heat. The electrode in the anode chamber should dip only half-way into the liquid. After about four hours stop the electrolysis and filter the liquid in the porous pot. The crystals thus obtained are dried on a porous plate. The filtrate is then re-saturated with ammonium sulphate, returned to the porous pot, and the electrolysis recommenced. The liquid in the cathode gradually becomes neutralized owing to the migration of the sulphuric acid anions out of it and the ammonium ions into it. Hence from time to time the acid must be replaced. The anode liquid becomes poorer in ammonia, and accumulates free acid. Hence after every two operations ammonia should be added to the anode liquid (gradually to prevent heating) until the acid is almost neutralized. At the first operation the separation of persulphate is small, since the solution has first to become saturated in respect to persulphate. In later operations the deposit commences almost immediately, and a good yield results. The current efficiency is 70 per cent., and

the yield 60 per cent. It is essential that the anode should be washed with water and heated to glowing before each experiment. The raw product contains about 5 per cent. ammonium sulphate. A pure specimen can be obtained (with considerable loss) by making quickly a saturated solution of the crude salt with water at $50^{\circ}\text{C}.$, and then cooled slowly to a low temperature. Ammonium persulphate is only stable when perfectly dry. The purity of the sample may be tested by pouring a solution (freshly made up) into a strongly acid solution of

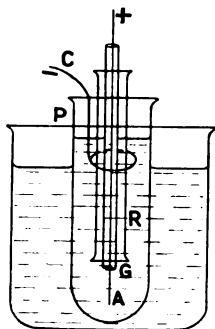


FIG. 71

ferrous ammonium sulphate and titrating the excess of ferrous salt with potassium permanganate. It must be remembered that the oxidation by persulphate takes several minutes to accomplish completely. In the preparation of persulphates, hydrogen peroxide and its derivatives are also formed in the anode chamber; these can be determined directly by permanganate. Hence, to follow the course of electrolysis, take a sample of the anode liquid titrate with permanganate, then add excess of acid ferrous ammonium sulphate. The first titration gives the peroxide content, and the second the persulphate content. Potassium persulphate may be similarly prepared, but the method is not quite satisfactory. In small quantity potassium persulphate can be easily prepared by the apparatus indicated in Fig. 71.

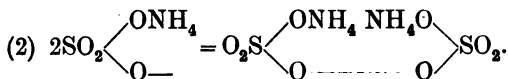
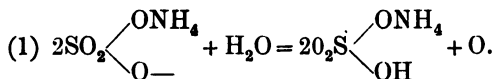
A wide boiling-tube, *P*, contains a saturated solution of potassium sulphate in sulphuric acid, of specific gravity 1.2 to 1.3.

The anode, *A*, consists of a platinum wire, a large portion of which is surrounded by a glass tube, into which the platinum is sealed. The wire (which must be ignited before use) passes almost to the bottom of the boiling-tube. A wider tube, *R*, surrounds the anode to carry away the oxygen liberated at the anode, without stirring up the liquid, which would prevent concentration at the anode. The cathode consists of a platinum loop, *C*, which passes outside to the tube *R*. The contents of the tube are kept cool by immersing the whole apparatus in a large beaker of cold water—use a current density of

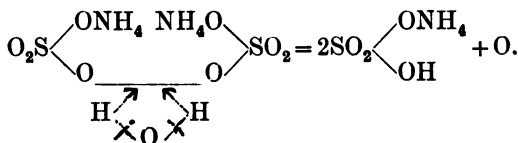
100 ampères per 100 sq. cms. at the anode, utilizing a current of 1 to 2 ampères. A thick deposit of potassium persulphate will form at the bottom of the vessel after ten minutes.

The formation of persulphates at the anode is explained by the fact that in concentrated solutions of sulphates, such as, say, ammonium sulphate, there are present HSO_4 anions as well as SO_4 anions, and the greater the concentration and current density the greater the extent to which they are discharged.

The discharged anions may react in two ways—



High current density favours the second reaction, hence high current densities are necessary for the formation of persulphates. The above graphic formula agrees with its properties—*i.e.*, the persulphates behave as derivatives of hydrogen peroxide. Upon warming an aqueous solution of the acid, or its salts, oxygen is evolved.



A low temperature is therefore necessary for their preparation.

CHAPTER XIX

PREPARATION OF COLLOIDS

A LARGE number of substances are capable of apparently dissolving in water to form what may be termed *pseudo-solutions*. Such pseudo-solutions are characterized by an extremely low diffusive power, a low osmotic pressure, and an inability to undergo dialysis; in these respects they differ from true solutions of crystalloids, and are therefore termed *colloidal solutions*. Such colloidal solutions are distinguished, according to the nature of the solvent, as hydrosols for water as a solvent, and alcosols when alcohol is the solvent. If the pseudo-dissolved substance is separated from the solvent, it is often found not to have lost the power of again passing into colloidal solution; such are termed *reversible colloids*. On the other hand, many substances, mainly inorganic, when separated from the solution do not possess the power of re-dissolving again except by some special process, such are termed *irreversible colloids*. Solutions of irreversible colloids can be obtained by Bredig's method, by disintegrating the substance in an electric arc under water, by double decomposition in aqueous solution, preventing precipitation by suitable means, or by previously imparting to the solid the ability to dissolve by treatment with small quantities of acid or alkali. This latter method is known as *peptization*, and has been employed to bring metallic oxides, etc., into a plastic condition for the formation of the so-called colloidal electric lamp filaments.

Many irreversible colloids separate out from their solutions as voluminous precipitates, containing a large amount of water; such are known as hydrogels, such are ferric oxide, aluminium oxide, etc. They contain far more water than is required for their hydrates, and are therefore frequently termed *oxide hydrogels*.

The change from the hydrosol state to that of the hydrogel can be very easily brought about by the addition of an electrolyte. Many colloidal solutions are exceedingly sensitive to electrolytes, hence an essential condition for their preparation is the entire absence of an electrolyte. A very characteristic property of colloids is their power of adsorption. Hence different dissolved colloids can combine together to form adsorption compounds. A gold hydrosol is exceedingly sensitive to electrolytes, but if a non-sensitive colloid, such as gelatine, is added, the gold solution remains stable towards small amounts of electrolyte. This would seem to indicate that some kind of combination had taken place between the two dissolved colloids. Such substances, which act like gelatine, are known as *protective colloids*.

On the other hand, certain colloids have the property of precipitating one another out of solution. Thus arsenic sulphide hydrosol and iron oxide hydrosol, when mixed in the correct proportions, are precipitated as a common adsorption compound. This is due to the fact that colloids carry a charge, and in this case the charges on the respective hydrosols are of opposite sign, hence they neutralize, and precipitation results. It is a rule that two such colloids, in order to precipitate each other, must have charges of opposite sign when referred to a common solvent.

The fact that colloids possess a charge explains why they are precipitated by electrolytes. The electrolyte dissociates, giving ions of opposite charges, and that which is opposite in sign to that of the pseudo-dissolved substance is adsorbed, and precipitation results. The passage of a colloidal solution through a narrow glass tube causes the precipitation of the colloid, simply because the charge is given up to the walls of the tube. When a colloidal solution is subjected to an electrical potential, the colloid "wanders" either to the anode or the cathode, according to its charge. Undoubtedly, then, the particles do carry charges, but the charges are small and the motion slow, and the number of moving particles small in comparison with an ordinary electrolyte. It is also uncertain whether the particles are discharged at the poles.

Preparation of Colloidal Platinum by Bredig's Method
—Take two pieces of platinum wire, about 1 mm. diameter and 10 to 15 cms. long, and insulate them by sealing them

into a glass tube so that about 3 cms. project. Then connect the other ends of the wire with 110-volt lighting circuit by means of binding screws, these junctions being insulated by "insulating tape," or, better, by a wider glass tube (see Fig. 72). Insert an ammeter and a resistance in the circuit. Take about 150 c.c. of distilled water in a glass dish, and clamp one electrode so that it dips below the surface of the water. Take the other in the hand and touch the first one, and then remove it a short distance, so as to maintain a small arc under water. A current of 6 to 10 amperes should be used, this being regulated by the resistance. Of course, care must be taken to see that the wiring will take such a current. It is not usually possible to maintain an arc for any length of time, so that when the arc breaks

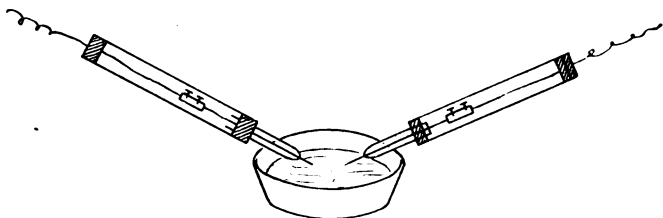


FIG. 72

it must be restarted by bringing the electrodes into contact again. This process is repeated until the solution becomes almost opaque or very hot. The solution thus obtained contains a considerable amount of coarse platinum powder. This is removed by filtering the solution. The filtrate then contains colloidal platinum.

Test the colloidal solution as follows :

1. Take a few cubic centimetres in a test-tube, and add a drop or two of an electrolyte (say KCl solution); after a time the colloid metal separates out.
2. To a few cubic centimetres of a dilute solution of hydrogen-peroxide add a few drops of the colloidal solution. Oxygen is evolved, due to the catalytic action of the platinum.

Preparation of Colloidal Antimony Sulphide—Prepare 100 c.c. of a 1 per cent. solution of tartar emetic, and place

it in a dropping funnel, and allow it to drop, drop by drop, into 100 c.c. hydrogen sulphide water, through which a moderately rapid stream of hydrogen sulphide is passing. Under these conditions no precipitate of antimony sulphide should be formed, but the antimony sulphide should remain in colloidal suspension as a deep orange-coloured pseudo-solution, which is perfectly clear when seen by transmitted light. The excess of hydrogen sulphide must now be removed by passing through the solution of pure hydrogen. The solution thus obtained is now *dialyzed*. This may be conveniently done by stretching a sheet of parchment over a wooden hoop, thus forming a sort of tambourine, and floating this in a basin of water (see Fig. 73). The solution is placed inside the drum, and the salts present in solution gradually diffuse through the orange-coloured material remaining on the parchment. Fresh quantities of distilled water are added to the colloid in the drum every three or four hours the first day, and later every twelve hours for four days, after which the colloidal solution will be free from foreign salts. The orange solution may then be transferred to a clean beaker.

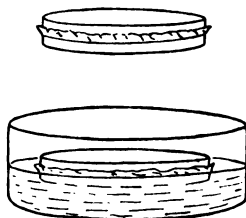


FIG. 73

Experiments with Colloidal Antimony Sulphide—Prepare approximately normal solutions of potassium chloride, barium chloride, and aluminium chloride. Take three separate portions of 10 c.c. each of the colloidal solution, and to each portion add one of the above standard solutions from a burette, and determine the amount of each of the above electrolytes, which will *just* completely precipitate the antimony from the solution. This should be done roughly at first, allowing the precipitate to settle after each addition, and noting the effect of the next addition in the supernatant liquid, which should gradually become colourless. The largest amount of electrolyte required will be in case of potassium chloride, and the smallest in the case of aluminium chloride. The precipitating power depending for this class of colloid on the valency of the cation—i.e., on its electrical charge.

Preparation of Colloidal Gold Solution by Donau's Method—Dissolve 0.25 gram of crystallized $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 500 c.c. of distilled water. Pass through this solution a *slow* stream of carbon monoxide, prepared from oxalic acid and strong sulphuric acid, passing the gas first through a solution of potassium hydroxide to remove the carbon dioxide. There is produced first a violet, then a reddish-violet, followed by a deep red coloration. Stop the reaction at this point. Preserve the solution for later experiments.

Preparation of Colloidal Stannic Oxide—To 5 c.c. of tin tetra chloride add 150 c.c. of distilled water, thus hydrolyzing it. Add this solution to 500 c.c. of distilled water, to which a few drops of ammonia have been added. Dialyze this solution for five days, changing the outside water, about three times a day until it shows no test for chlorides. It is quite probable that the *hydrogel* may to some extent result. The contents of the dialyzer are transferred to a beaker, and the gel *peptised* by the addition of three or four drops of ammonia. After a time the jelly will completely disappear, leaving a perfectly clear *hydrosol*.

A pseudo-solution of zircon oxide may be similarly prepared by dialyzing for five days a 15 per cent. solution of zircon nitrate.

The ferric oxide hydrosol may be prepared from dilute ferric chloride similarly.

Experiments—(1) To 2 c.c. of the colloidal gold solution add 2 c.c. of the stannic oxide hydrosol; no change occurs. Now add a little ammonium chloride solution; a beautiful deep reddish purple precipitate is formed, which has the characteristic property of being soluble in ammonia. In this experiment we have synthesized the *Purple of Cassius*.

(2) Take 75 c.c. of a boiling colloidal gold solution and add 15 c.c. of boiling zircon hydrosol solution; a zircon-gold-purple precipitate results in this case without the addition of an electrolyte. The precipitation takes place slowly in the cold.

(3) Take 10 c.c. of the colloidal gold solution and add a few drops of hydrochloric acid; a blue coloration first results, followed by a deposit of the metal. Take a further 10 c.c. of the gold hydrosol solution and add 1 drop of a 2 per cent. solution of gelatine, and again add a little hydrochloric acid. In this case there is neither change of colour nor a deposit of the metal. Here we have an example of a *protective colloid*.

APPENDIX

TABLE OF RELIABLE MELTING AND BOILING-POINTS

Liquid Hydrogen	...	...	...	...	...	- 253°
Liquid Oxygen	...	...	...	...	...	- 182°
Freezing Mercury	...	...	...	...	...	- 39°
Melting Ice	...	...	...	...	...	0°
Boiling-point of Aniline at 760 mm. pressure	...	...	...	...	...	184°
" " Naphthalene	...	...	...	...	...	220°
" " Diphenylamine	...	...	...	...	...	302°
" " Sulphur	...	...	...	...	...	445°
Melting-point of Tin	...	...	...	...	...	232°
" " Zinc	...	...	...	...	...	419°
" " Antimony	...	...	...	...	...	632°
" " Aluminium	...	...	...	...	...	657°
" " Sodium Chloride	...	...	...	...	...	800°
" " Silver (in air)	...	...	...	...	...	955°
" " Silver (in reducing atmosphere)	...	...	...	...	...	962°
" " Gold	...	...	...	...	...	1064°
" " Copper (in air)	...	...	...	...	...	1062°
" " Potassium Sulphate..	...	...	...	...	...	1070°
" " Copper (in reducing atmosphere)	...	...	...	...	...	1084°
" " Nickel	...	...	...	...	...	1427°
" " Pure Iron	...	...	...	...	...	1503°
" " Palladium	...	...	...	...	...	1545°
" " Platinum	...	...	...	...	...	1750°
Boiling-point at 760 mm. pressure of Magnesium	...	...	...	...	...	1120°
" " " " Antimony	...	...	...	...	...	1440°
" " " " Lead	...	...	...	...	...	1525°
" " " " Aluminium	...	...	...	...	...	1800°
" " " " Manganese	...	...	...	...	...	1900°
" " " " Silver	...	...	...	...	...	1955°
" " " " Chromium	...	...	...	...	...	2200°
" " " " Tin	...	...	...	...	...	2270°
" " " " Copper	...	...	...	...	...	2310°
" " " " Iron	...	...	...	...	...	2450°

DENSITY OF WATER

Temperature	Density	Temperature	Density
0°	0.99987	21°	0.99802
1°	0.99993	22°	0.99779
2°	0.99997	23°	0.99756
3°	0.99999	24°	0.99732
4°	1.00000	25°	0.99707
5°	0.99999	26°	0.99681
6°	0.99996	27°	0.99654
7°	0.99993	28°	0.99626
8°	0.99988	29°	0.99597
9°	0.99981	30°	0.99567
10°	0.99973	31°	0.99537
11°	0.99963	32°	0.99505
12°	0.99953	33°	0.99473
13°	0.99940	34°	0.99440
14°	0.99927	35°	0.99406
15°	0.99913	40°	0.99224
16°	0.99897	50°	0.98807
17°	0.99880	60°	0.98324
18°	0.99862	70°	0.97781
19°	0.99843	80°	0.97183
20°	0.99823	90°	0.96534

VAPOUR PRESSURES OF WATER

Temperature	Vapour Pressures	Temperature	Vapour Pressures
	Mm.		Mm.
4°	6.1	19°	16.5
5°	6.5	20°	17.5
6°	7.0	21°	18.7
7°	7.5	22°	19.8
8°	8.0	23°	21.1
9°	8.6	24°	22.4
10°	9.2	25°	23.8
11°	9.8	26°	25.2
12°	10.5	27°	26.7
13°	11.2	28°	28.4
14°	12.0	29°	30.1
15°	12.8	30°	31.8
16°	13.6	31°	33.7
17°	14.5	32°	35.7
18°	15.5	33°	37.7

VISCOSITY AND SURFACE TENSION OF WATER

Temperature	Viscosity	Surface Tension	Temperature	Viscosity	Surface Tension
10°	—	74·05	35°	0·00724	—
15°	—	73·26	35°	—	70·29
15°	0·01142	—	40°	—	69·54
20°	—	72·53	40°	0·00657	—
20°	0·01006	—	45°	—	68·6
25°	0·008926	—	45°	0·00600	—
25°	—	71·78	50°	—	67·8
30°	—	71·03	50°	0·005500	—
30°	0·00800	—			

PHYSICAL DATA FOR BENZENE

Temperature	Density	Viscosity	Surface Tension
0°	0·9006	—	—
11·4°	—	—	28·83
14·8°	—	0·007038	—
20°	0·8790	—	—
30·8°	—	0·005522	—
31·2°	—	—	26·68
40°	0·8576	—	—
46·9°	—	0·004435	—
55·1°	—	—	23·53
60°	0·8357	—	—
68·5°	—	—	21·70
70°	0·8247	—	—
78·3°	—	—	20·51
78·8°	—	0·003177	—

DENSITY OF PURE ALCOHOL

Temperature	Density	Temperature	Density
10°	0·7979	40°	0·7722
20°	0·7894	50°	0·7633
30°	0·7810		

DEGREES OF IONIZATION OF SOME
ELECTROLYTES AT 18°

Electrolytes	N	$\frac{\kappa}{10}$	Electrolytes	N	$\frac{\kappa}{10}$
CuSO ₄	0.21	0.38	KI	0.79	0.86
AgNO ₃	0.58	0.81	KNO ₃	0.63	0.83
ZnSO ₄	0.23	0.39	NaCl	0.68	0.84
KCl	0.76	0.86	HCl	0.71	0.92
KBr	—	0.86			

EQUIVALENT CONDUCTIVITY OF INFINITE
DILUTION

Tempera- tures	Electrolytes	Conduc- tivity	Tempera- tures	Electrolytes	Conduc- tivity
18°	NaCl	108.99	18°	KCNS	121.30
18°	NaNO ₃	105.33	18°	KClO ₃	119.70
18°	KCl	130.10	18°	AgNO ₃	115.80
18°	KBr	132.30	25°	Acetic Acid	389
18°	KNO ₃	126.50	25°	Benzoic Acid	381

DISCHARGE VOLTAGES OF DIFFERENT IONS
FROM AQUEOUS SOLUTIONS

On reversing the signs, the values represent the solution tendency.

(a) Cation discharge points.

Cation	Volts	Cation	Volts
K'	$-2.92 + \frac{1}{n} (0.058 \log_{10} C)$	Ni''	$+0.06 + \frac{1}{n} (0.058 \log_{10} C)$
Na'	$-2.52 + ,, ,,$	Pb''	$+0.16 + ,, ,,$
Mg''	$-1.27 + ,, ,,$	Sn''	$+0.18 + ,, ,,$
Zn''	$-0.48 + ,, ,,$	H'	$+0.277 + ,, ,,$
Fe''	$-0.15 + ,, ,,$	Cu''	$+0.62 + ,, ,,$
Cd''	$-0.12 + ,, ,,$	Ag'	$+1.08 + ,, ,,$
Tl'	$-0.04 + ,, ,,$	Hg''	$+1.14 + ,, ,,$
CO''	$-0.01 + ,, ,,$	Au'	$+1.78 + ,, ,,$

(b) Anion discharge points.

$$S' = -0.28 + \frac{1}{n} (0.058 \log_{10} C)$$

$40H' \rightarrow O_2 + 2H_2O$	0.69 +	"	"
I'	0.82 +	"	"
Br'	1.36 +	"	"
Cl'	1.63 +	"	"
F'	2.18 +	"	"

C = Ionic concentration at 25°.

n = Valency.

SPECIFIC HEATS AND ELECTRICAL RESISTANCES AT 0°

	Specific Heat	Specific Resistance
Aluminium	0.22	0.028×10^{-4}
Iron	0.11	$0.99 - 0.15 \times 10^{-4}$
Copper	0.093	0.017×10^{-4}
Nickel	0.11	$0.08 - 0.11 \times 10^{-4}$
Platinum	0.032	$0.108 - 0.11 \times 10^{-4}$
Silver	0.056	0.016×10^{-4}
Mercury	0.0332	0.958×10^{-4}
Glass	0.19	1.0×10^{-15}
Graphite	0.155	14.3×10^{-4}
Retort carbon	0.165	49.0×10^{-4}

LIQUID PLATINUM

Moisten 0.3 gram of platinic chloride with conc. HCl, and mix with 1 c.c. of conc. boric acid solution. Dissolve in alcohol and add 1 c.c. of French turpentine, and 2 c.c. of oil of lavender.

NERNST LIQUID RESISTANCE

The Nernst liquid resistance, suitable for conductivity work, consists of 121 grams of mannite, 41 grams of boric acid and 0.06 gram KCl in a litre of aqueous solution. $K = 0.00097$ at 18°, and temperature coefficient is exceedingly small.

TABLOID PRESS

A suitable form of press for making compressed tabloids, as required for combustion experiments, etc., is as shown in Fig. 73. It consists of a mould, *M*, the two halves being

joined by a hinge on one side and secured by a winged nut on the other. The substance of which a tabloid is required is placed in the mould (in the case of hard substances like coal they should be finely powdered) and a plunger inserted. The mould is then placed in the screw press, as indicated in Fig. 74,

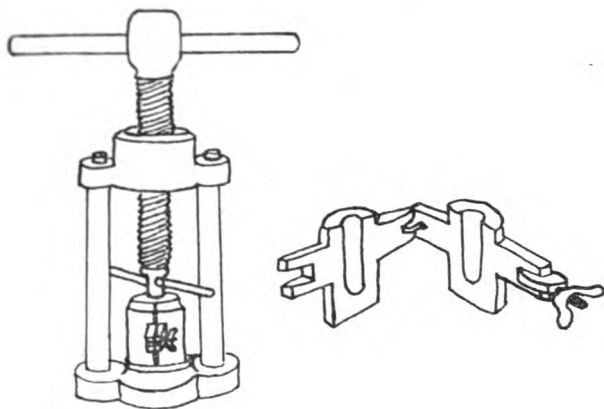


FIG. 74

and the screw turned as far as possible, thus exerting great pressure on the substance. The pressure is then relieved, and then by undoing the winged nut the mould can be opened and the tabloid removed. In order to make a tabloid successfully, the groove of the mould must be perfectly clean, and kept as smooth as possible.

DETERMINATION OF MOLECULAR WEIGHTS BY THE ELEVATION OF BOILING-POINT AND DEPRES- SION OF THE FREEZING-POINTS (BECKMANN'S METHOD)

1. VALUES OF K FOR BOILING-POINT METHOD

Solvent	Boiling-Point	K
Ether	34.9°	2110
Carbon disulphide	46.2°	2370
Acetone	56.3°	1670
Chloroform	61.2°	3660
Ethyl acetate	74.6°	2610
Ethyl alcohol	78.3°	1150
Benzene	80.3°	2670
Water	100.0°	520
Acetic acid	118.1°	2530

2. VALUES OF K FOR FREEZING POINT METHOD

Solvent	Freezing-Point	K
Water	0°	1860
Acetic acid	17°	3860
Benzene	5.5°	5000

LATENT HEATS

Solvent	Vaporization	Fusion
Water	535.9°	79.1°
Acetic acid	—	48.1°
Benzene	92.9°	30.1°
Ether	0.90°	—
Acetone	125.3°	—
Ethyl alcohol	215.0°	—

VALUES OF K (LANDSBERGER'S METHOD)

Solvent	K	Solvent	K
Alcohol	1560	Acetone	2220
Ether	3030	Chloroform	2600
Water	540	Benzene	3280

Note—The values of K in Beckmann's Method are for 1 gram of solvent, whereas those for Landsberger's Method are for 1 c.c. of solvent. In the former case the weight of the solvent is known, and the latter case the volume.

VALUES OF μ_{∞} at 25° C. (SEE CONDUCTIVITY)

Acid	μ_{∞}	K=100 κ
Acetic acid	389	1.8×10^{-3}
Succinic acid	381	6.65×10^{-3}
Benzoic acid	381	6.0×10^{-3}
Mandelic acid	378	4.17×10^{-2}

DENSITY OF ACETONE

Density (15°/4°)=0.7971

INTERNATIONAL ATOMIC WEIGHTS, 1914

Element	Symbol	Atomic Weight	Element	Symbol	Atomic Weight
Aluminium ...	Al	27·1	Neon ...	Ne	20·2
Antimony ...	Pb	120·2	Nickel ...	Ni	58·68
Argon ...	A	39·88	Niobium ...	Nb	93·5
Arsenic ...	As	74·96	Niton ...	Nt	224·4
Barium ...	Ba	137·37	Nitrogen ...	N	14·01
Beryllium ...	Be	9·1	Osmium ...	Os	190·9
Bismuth ...	Bi	208·0	Oxygen ...	O	16·0
Boron ...	B	11·0	Palladium ...	Pd	106·7
Bromine ...	Br	79·92	Phosphorus ...	P	31·04
Cadmium ...	Cd	112·40	Platinum ...	Pt	195·2
Cæsium ...	Cs	132·81	Potassium ...	K	39·10
Calcium ...	Ca	40·07	Praseodymium	Pr	140·6
Carbon ...	C	12·0	Radium ...	Ra	226·4
Cerium ...	Ce	140·25	Rhodium ...	Rh	102·9
Chlorine ...	Cl	35·46	Rubidium ...	Rb	88·45
Chromium ...	Cr	52·0	Ruthenium ...	Ru	101·7
Cobalt ...	Co	58·97	Samarium ...	Sa	150·4
Copper ...	Cu	63·57	Scandium ...	Sc	44·1
Dysprosium ...	Dy	162·5	Selenium ...	Se	79·2
Erbium ...	Er	167·7	Silicon ...	Si	28·3
Europium ...	Eu	152·0	Silver ...	Ag	107·88
Fluorine ...	F	19·0	Sodium ...	Na	23·0
Gadolinium ...	Gd	157·3	Strontium ...	Sr	87·68
Gallium ...	Ga	69·9	Sulphur ...	S	32·07
Germanium ...	Ge	72·5	Tantalum ..	Ta	181·5
Gold ...	Au	197·2	Tellurium ...	Te	127·5
Helium ...	He	3·99	Terbium ...	Tb	159·2
Holmium ...	Ho	163·5	Thallium ...	Tl	204·0
Hydrogen ...	H	1·008	Thorium ...	Th	232·4
Indium ...	In	114·8	Thulium ...	Tm	168·5
Iodine ...	I	126·92	Tin ...	Sn	119·0
Iron ...	Fe	55·84	Titanium ...	Ti	48·1
Krypton ...	Kr	88·92	Tungsten ...	W	184·0
Lanthanum ...	La	139·0	Uranium ...	U	238·5
Lead ...	Pb	207·10	Vanadium ...	V	51·0
Lithium ...	Li	6·94	Xenon ...	Xe	130·2
Lutecium ...	Lu	174·0	Ytterbium (Neo-		
Magnesium ...	Mg	24·32	ytterbium) ...	Yb	172·0
Manganese ...	Mn	54·93	Yttrium ...	Y	89·0
Mercury ...	Hg	200·6	Zinc ...	Zn	65·37
Molybdenum ...	Mo	96·0	Zirconium ...	Zr	90·6
Neodymium ...	Nd	144·3			

Number	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0258	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3484	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	11
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	12
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
		2	3	4	5	6	7	8	9		1	2	3	4	5	6	7	8	9

Num- ber	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8

Log.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
16	1445	1448	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
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